How to Study ??

#1 Video

6 hr

#2 6 hr Ques practice

#2 Single Source

#3 Test Series → Analysis

Organic Chemistry

1. Basics of organic chemistry
2. IUPAC Nomenclature
3. Isomerism
4. GOC
5. Hydrocarbon
6. Haloalkane & Haloarene ✓
7. Alcohol phenol Ether ✓
8. Aldehyde ketone Carboxylic acid ✓
9. Amine ✓
10. Biomolecule ✓
11. practical chemistry

Basics of organic chemistry

Chemical comp

organic comp

Compounds obtained from living organisms.

eg → Plants
Animals

Inorganic comp

Comp obtained from non-living things

eg → Soil
Rocks
Minerals

बाबा **Berzilius Theory** VFT

* Ac to Berzilius, organic comp cannot be prepared in laboratory, by normal humans.
* Organic Comp can only exist due to Vital force / mysterious force / strong external force.
* This is also vital Force Theory (VFT)
* organic comp cannot be prepared from Inorganic Comp.

Wholar Synthesis

Wholar accidently prepared organic comp in laboratory. (Urea)

$$(NH_4)_2SO_4 + KCNO \longrightarrow NH_4CNO \xrightarrow{\Delta} NH_2-\overset{O}{\overset{\|}{C}}-NH_2$$

$2NH_4^+$ K^+

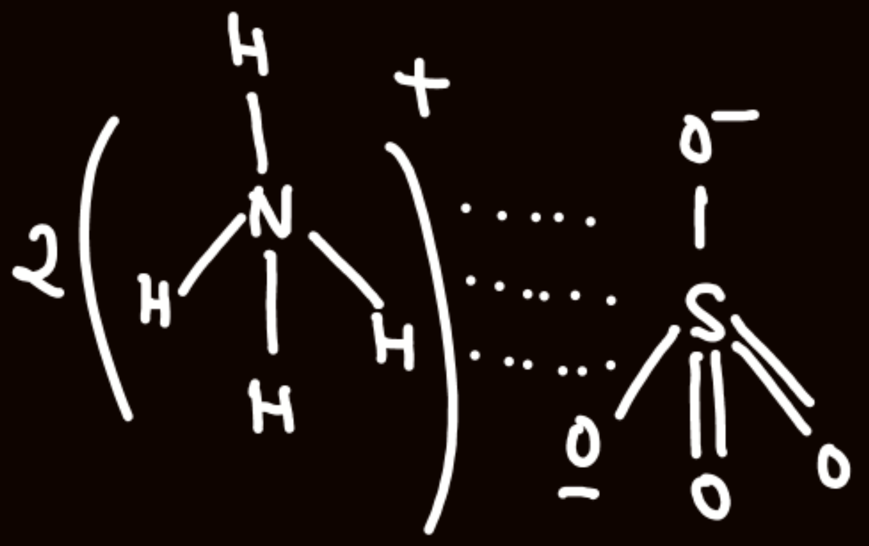
SO_4^{-2} CNO^-

Ammonium Sulphate   Potassium cyanate

NH_4CNO — Expected product — Ammonium cyanate

Urea — First organic Comp

Covalent bond

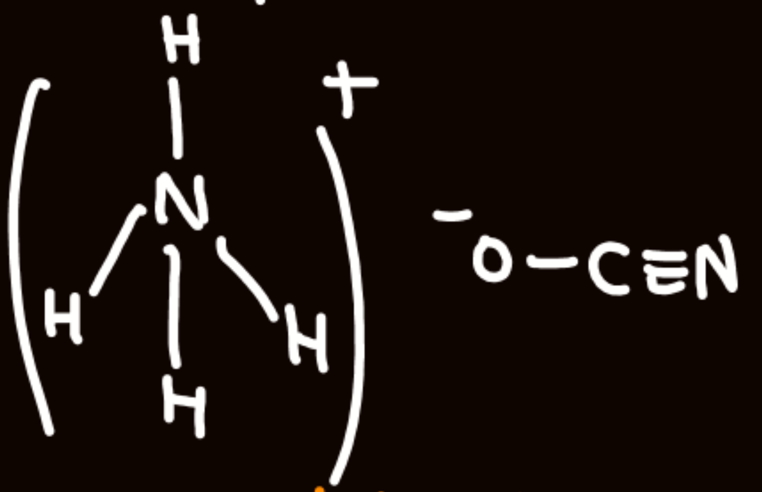


Ionic bond
Covalent bond
Cordinate bond

$\overset{+}{K}\ \overset{-}{O}-C\equiv N$

Ionic bond
Covalent bond

$NH_4^+\ CNO^-$



Ionic bond
Covalent bond
Cordinate bond

note →

A	K
U	W
M	B

Acetic Acid → Kolbe

Urea → Wholar

Methane → Berthelott

Modern Concept of organic Compound

organic Comp → Organic Compounds are Hydrocarbon or their derivatives.

Hydrocarbon: Compounds made of Carbon and Hydrogen.

derivatives: Remove H and add other elements

ex →

CH_4	$CH_2=CH_2$
C_2H_6	$CH\equiv CH$
C_3H_8	$CH_2=C=CH_2$
C_4H_{10}	CH_3-CHO
C_5H_{12}	$CH_3-C\equiv N$
CH_3NH_2	$C_6H_{12}O_6$
$C_{12}H_{12}O_{11}$	CH_3-OH
C_2H_5OH	CH_3Cl
CH_2Cl_2	$CHCl_3$
CCl_4	

CO_2 ✗

CS_2 ✗

H_2O ✗

HCN ✗

NOTE → Almost all organic comp are made up of carbon.

Therefore study of Carbon is Modern Concept of Organic Comp

4 characteristics of Carbon

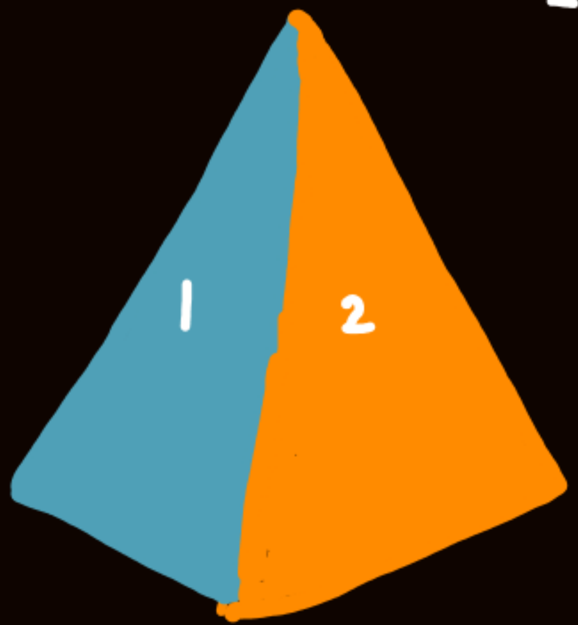
① Tetravalency → Carbon Forms 4 Covalent Bond (4 diff Sigmabond)

(6) C → $1s^2\ 2s^2\ 2p^2$ [1⇂] (2s) [1|1|] (2p)

C^* → [1] (2s) [1|1|1] (2p) } → (4 diff Sigmabond)

② Tetrahedral str (Symmetrical) → Stable Str ↓ 4 Face

(Tetra ↑ 4, hedral ↑ Face)



③ Tendency to form multiple bond –

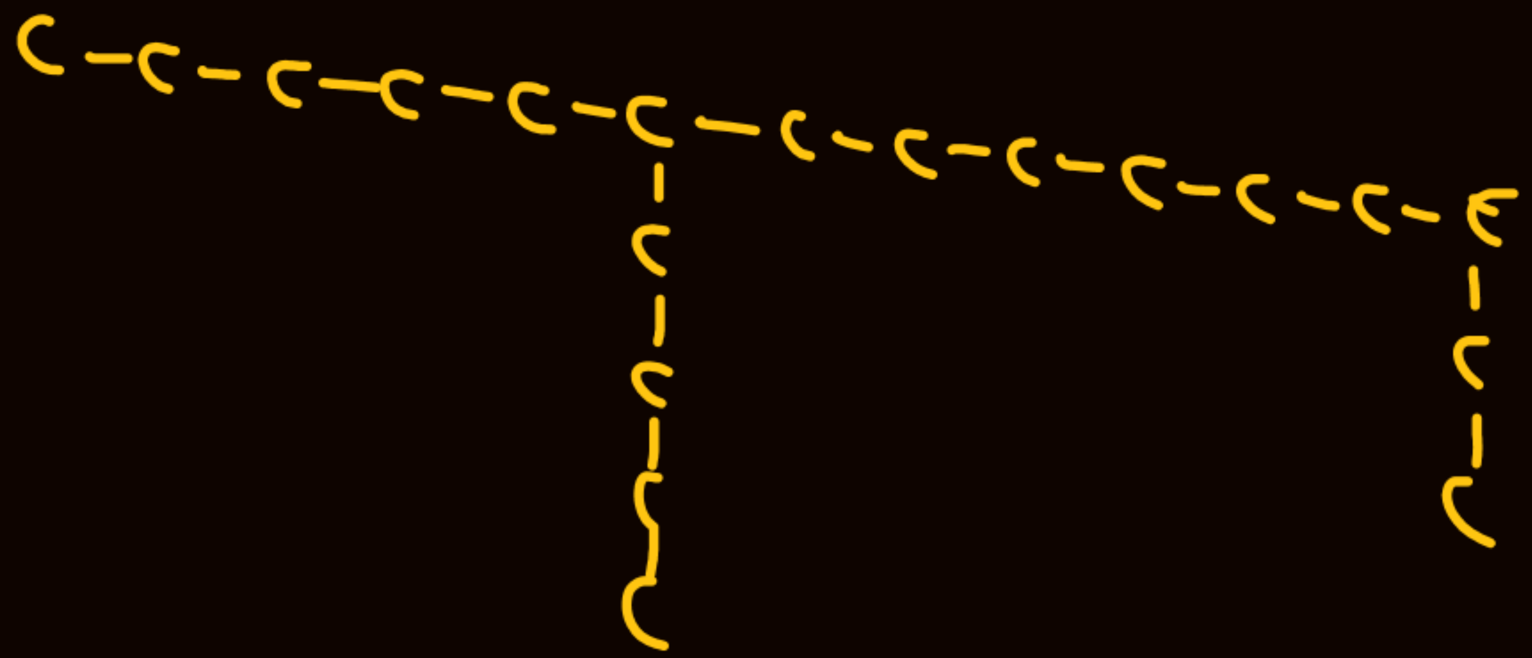
C–C
C=C
C≡C

C=C=C–C
C=C–C=C
C≡C–C≡C
C–C–C–C

C=C–C≡C
C=C–C≡C–C=C

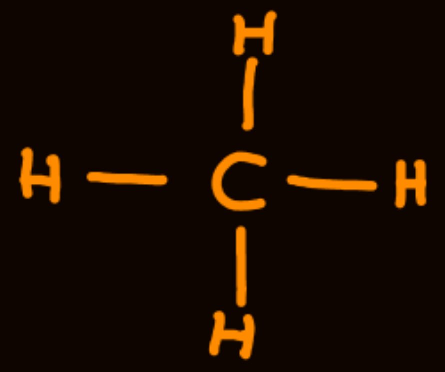
④ Tendency to show catenation – Carbon has self linking tendency to form long chain.

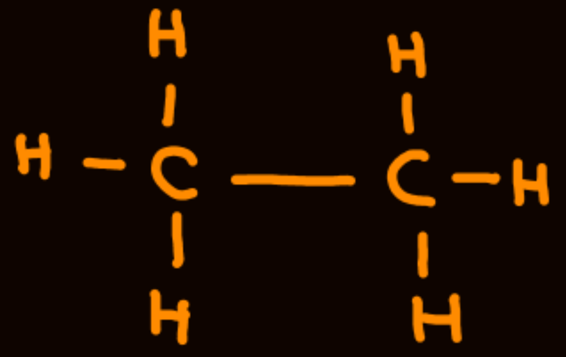
C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–

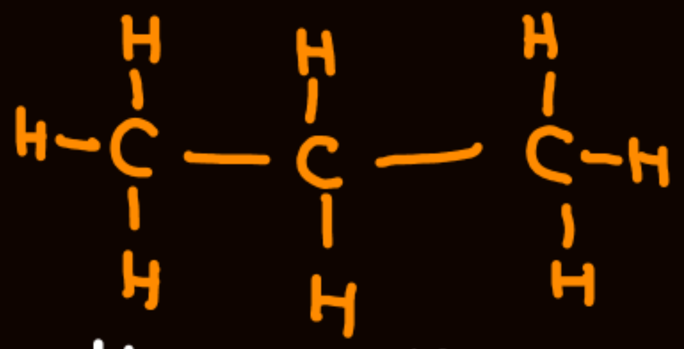


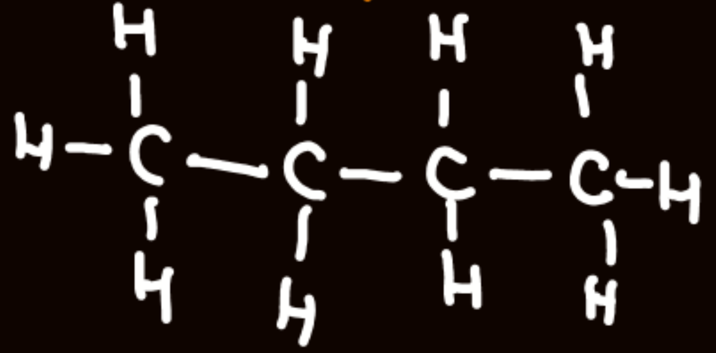
Structural Representation of organic Comp

Complete Representation









Condensed Representation

CH_4

CH_3-CH_3
or
CH_3CH_3

$CH_3-CH_2-CH_3$

$CH_3CH_2CH_3$

$CH_3-CH_2-CH_2-CH_3$

$CH_3CH_2CH_2CH_3$

$CH_3(CH_2)_2CH_3$

Bond Line Representation

→ C–H bond is not shown.

→ C–C " " shown by Zig-Zag line

→ Hydrogen of other atom is always shown.

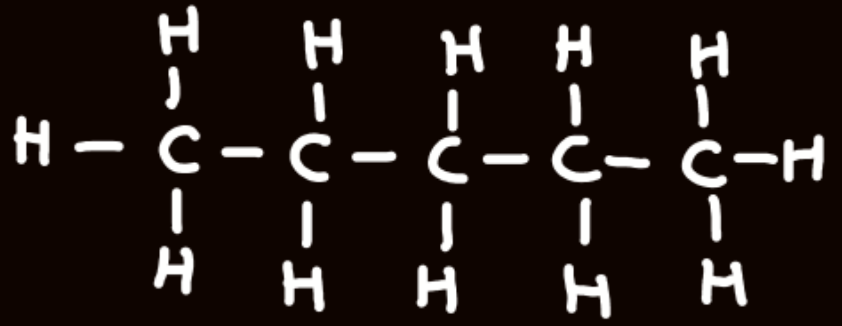


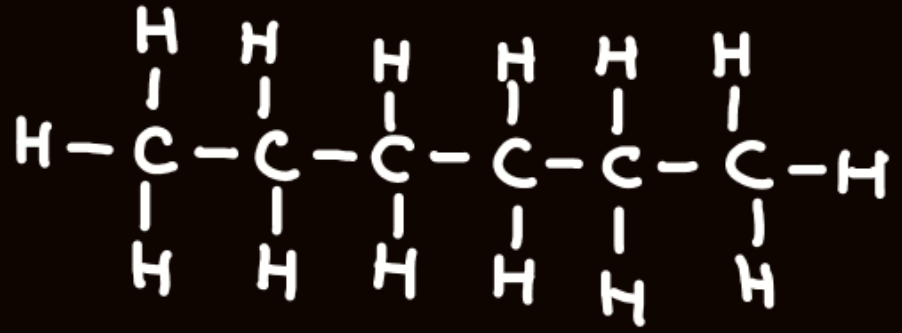


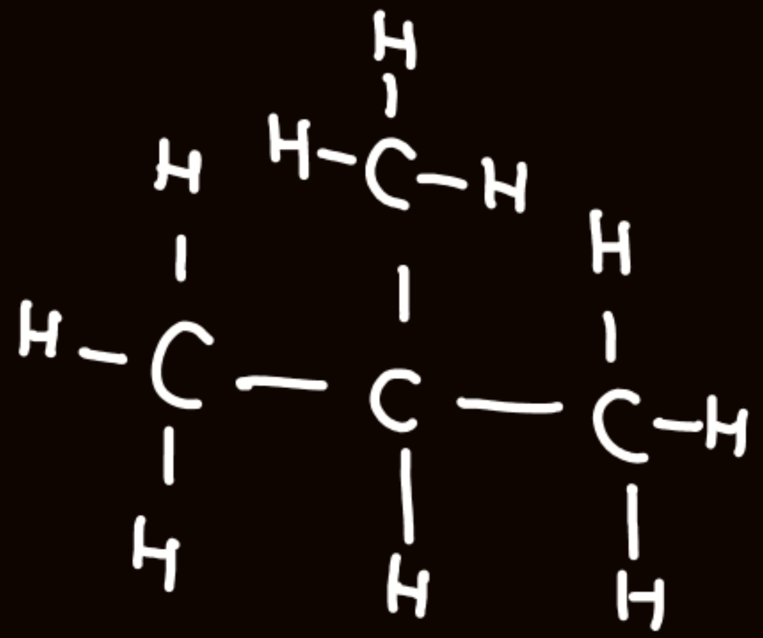


Structural Representation of organic Comp

Complete Representation







Condensed Representation

$CH_3-CH_2-CH_2-CH_2-CH_3$

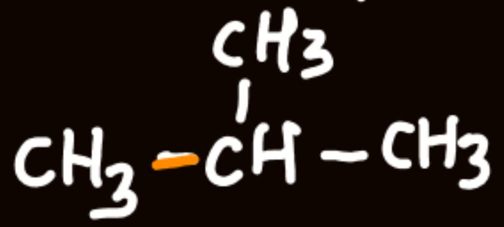
$CH_3CH_2CH_2CH_2CH_3$

$CH_3(CH_2)_3CH_3$

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

$CH_3CH_2CH_2CH_2CH_2CH_3$

$CH_3(CH_2)_4CH_3$



$CH_3CH(CH_3)CH_3$

$CH_3CH(CH_3)_2$ / $CH(CH_3)_3$

Bond Line Representation

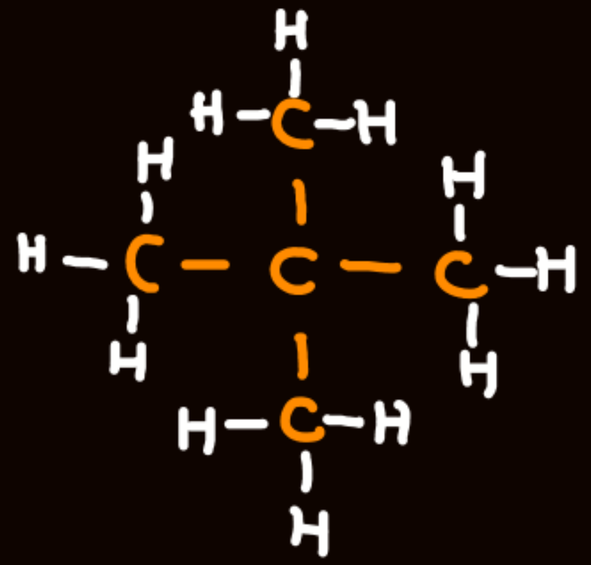


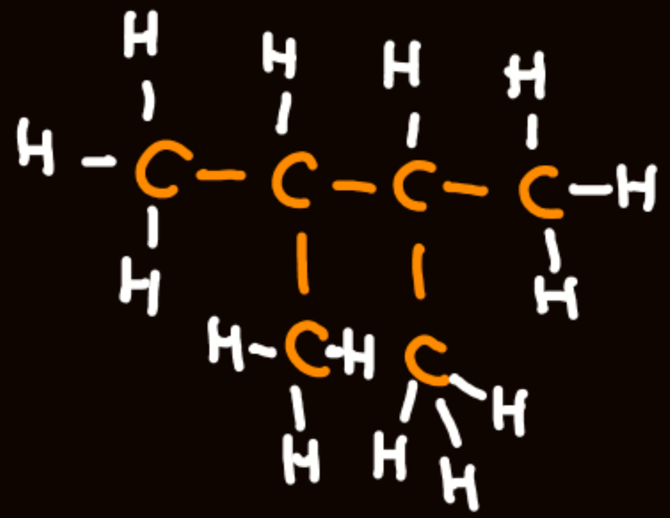




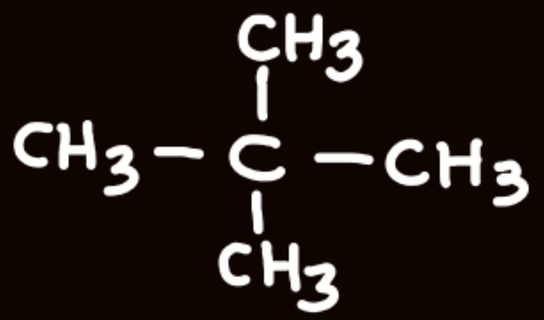
Structural Representation of organic Comp

Complete Representation





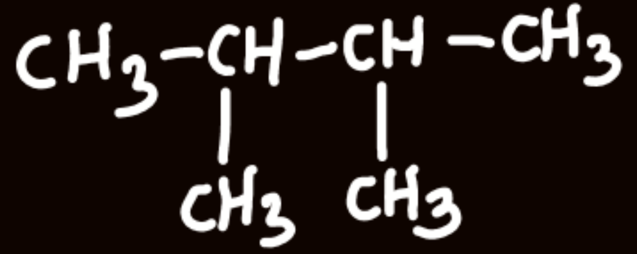
Condensed Representation



$CH_3C(CH_3)_2CH_3$

$CH_3C(CH_3)_3$

$C(CH_3)_4$

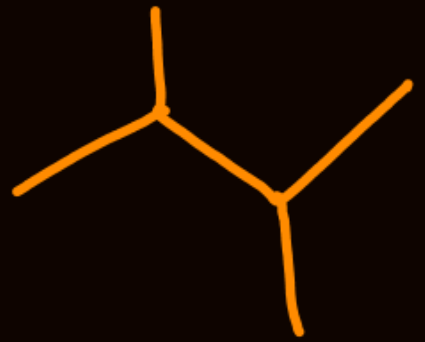


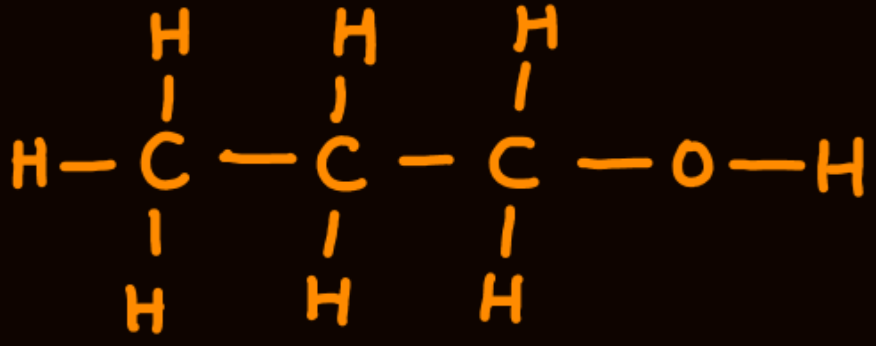
$CH_3CH(CH_3)CH(CH_3)CH_3$

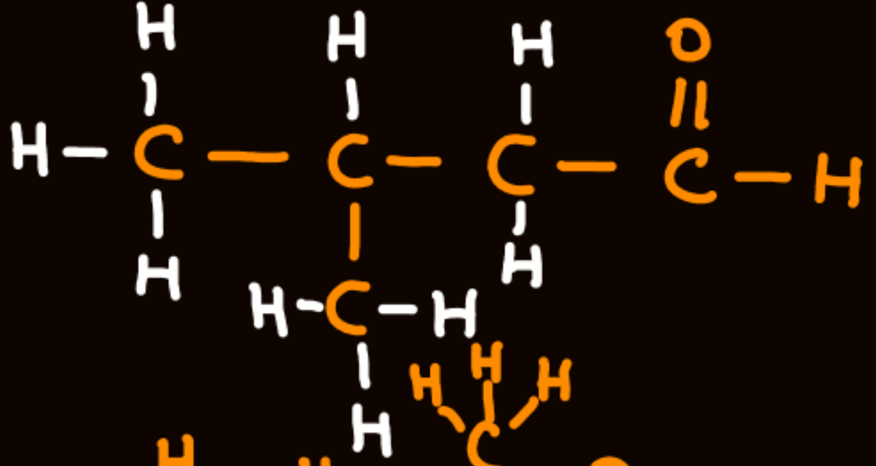
$CH_3CH(CH_3)CH(CH_3)_2$

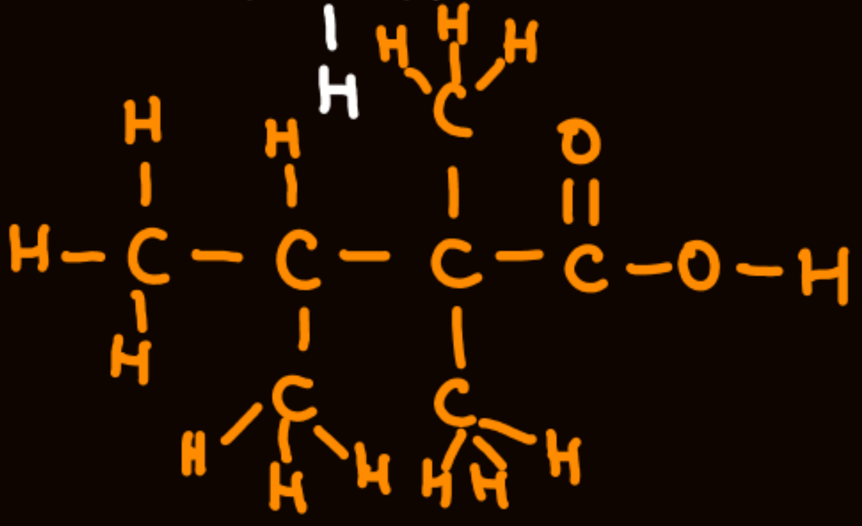
Bond Line Representation



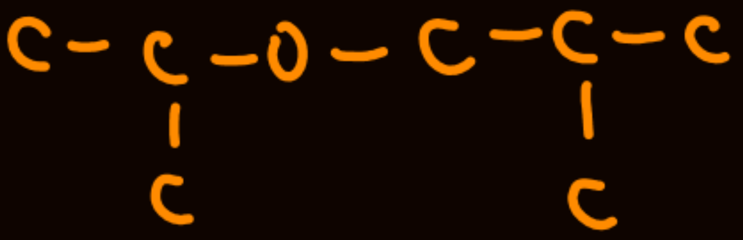








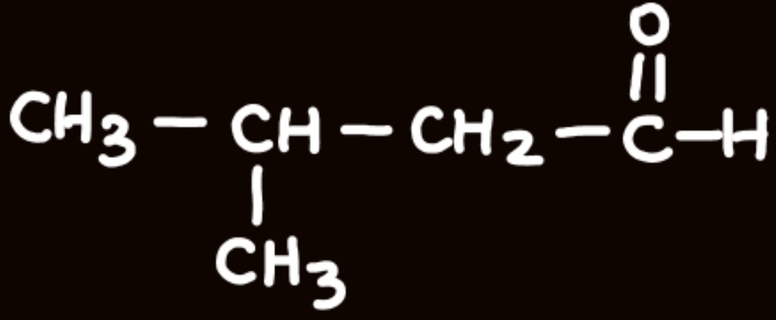
HW



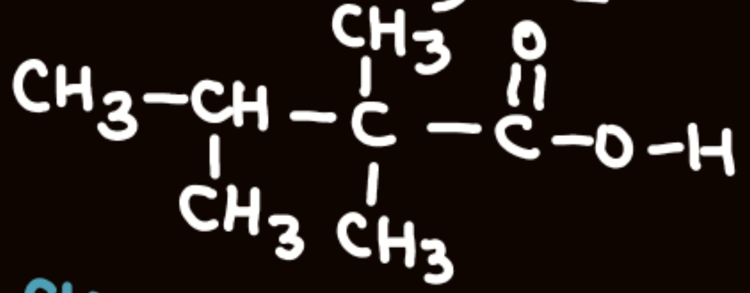
$CH_3-CH_2-CH_2-OH$

$CH_3CH_2CH_2OH$

$CH_3(CH_2)_2OH$

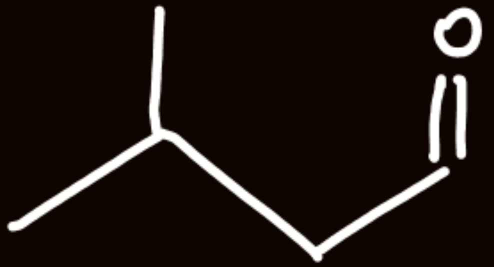


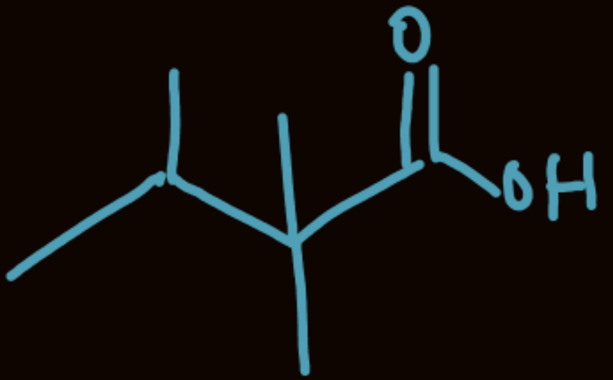
$CH_3CH(CH_3)CH_2CHO$



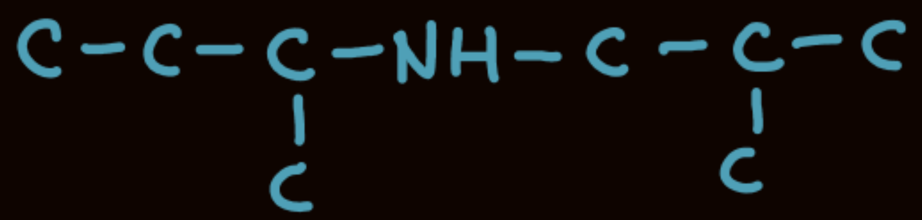
$CH_3CH(CH_3)C(CH_3)_2COOH$





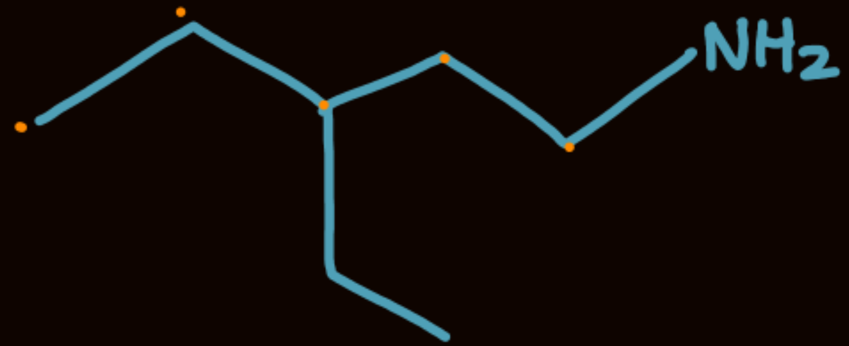


(Hw)



(Hw)

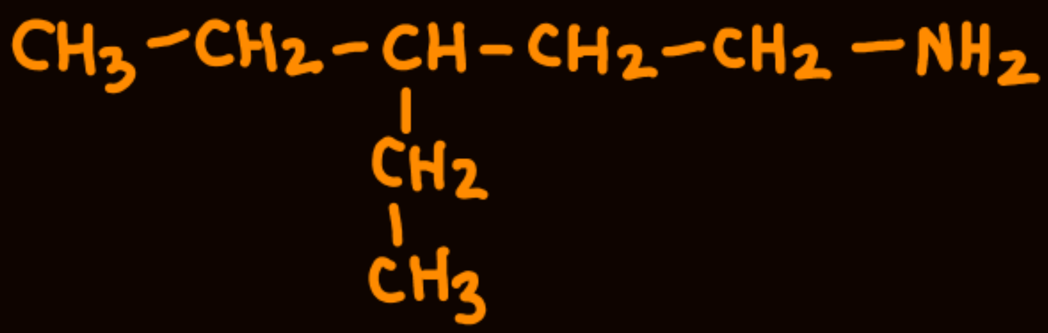
Que write the condensed formula -

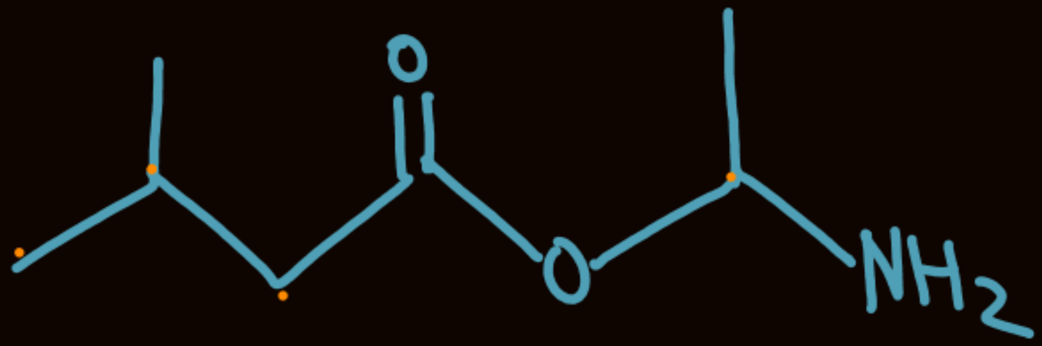


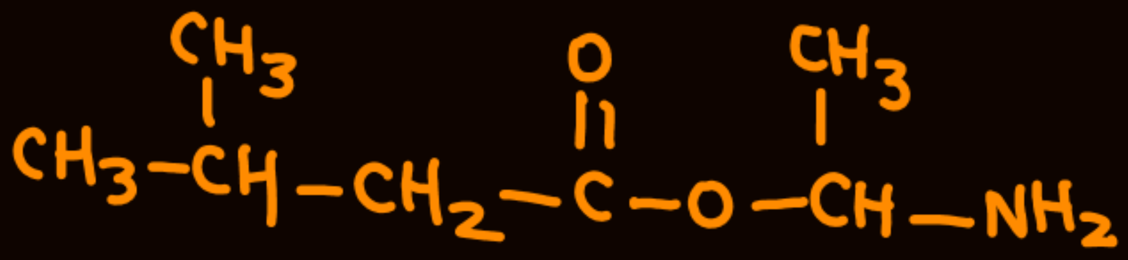
$CH_3CH_2CH(CH_2CH_3)CH_2CH_2NH_2$

$CH_3CH_2CH(CH_2CH_3)(CH_2)_2NH_2$

↑







$CH_3CH(CH_3)CH_2COOCH(CH_3)NH_2$

Life Lesson

Basics of OC

L1
- Old Concept
- Modern "
- Structural Representation of OC

L2
- σ bond, π bond, lp calc^{n}
- Hybridz^{n}
- Degree
- DU/DBE/IHD
- Classification of OC

doublebond
C=C → 1σ, 1π

Sigmabond = Single bond

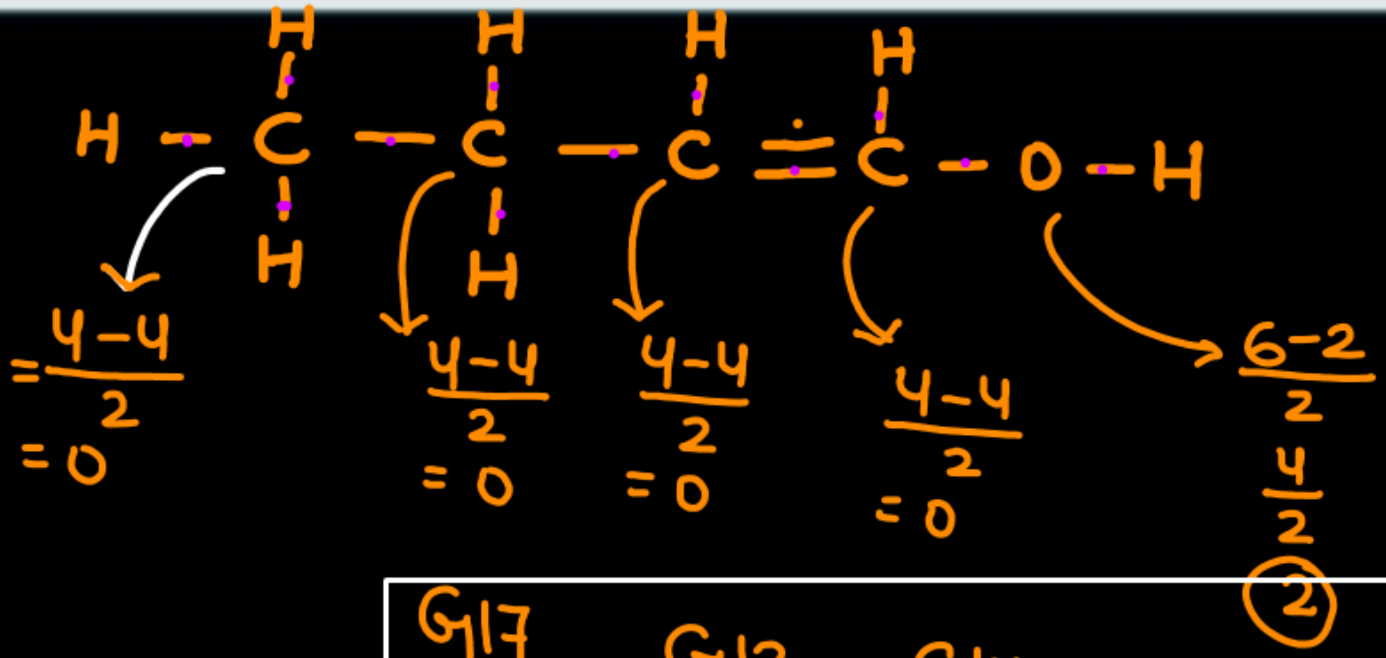
C≡C Triple bond = 1σ, 2π

lonepair = $\frac{\text{Valence } e^- - \text{bond}}{2}$

QUESTION:- Calculate number of sigma (σ) & pi (π) bond in the following :

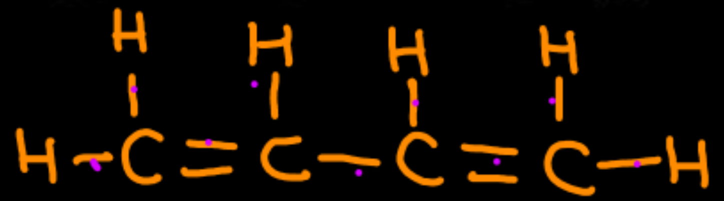
(i) $CH_3CH_2 - CH = CH - OH$

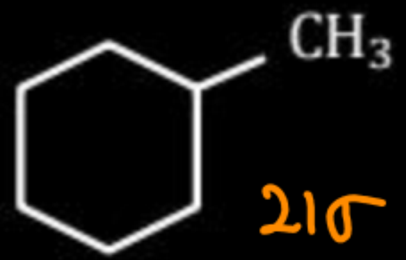
12σ 1π 2lp



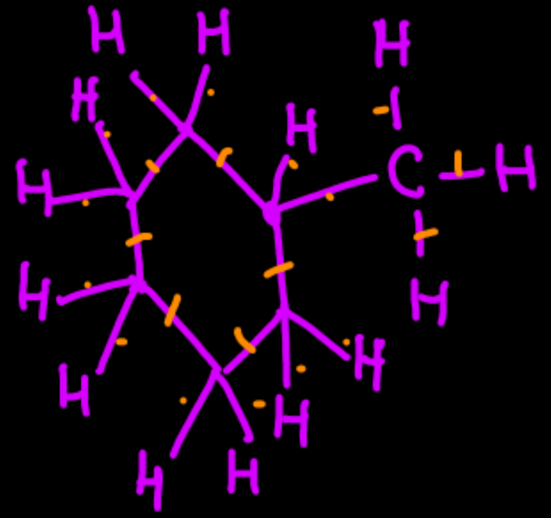
(ii) $CH_2 = CH - CH = CH_2$

9σ
2π
0lp



(iii) 

21σ
0π
0lp



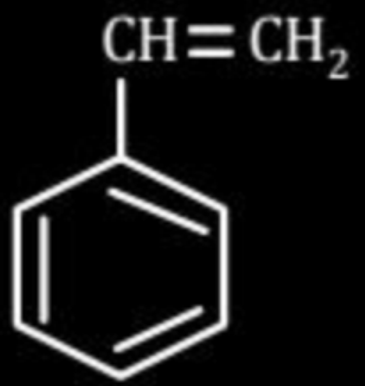
G17 → Halogen family 7

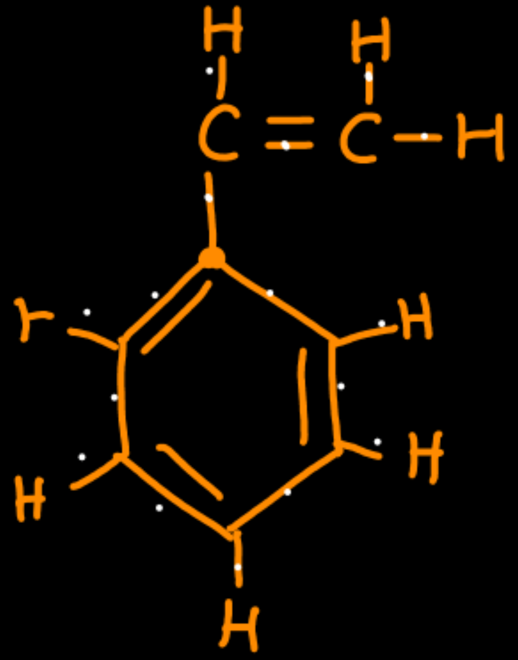
G13 → Boron Family → Ve = 3

G14 → carbon Family Ve = 4

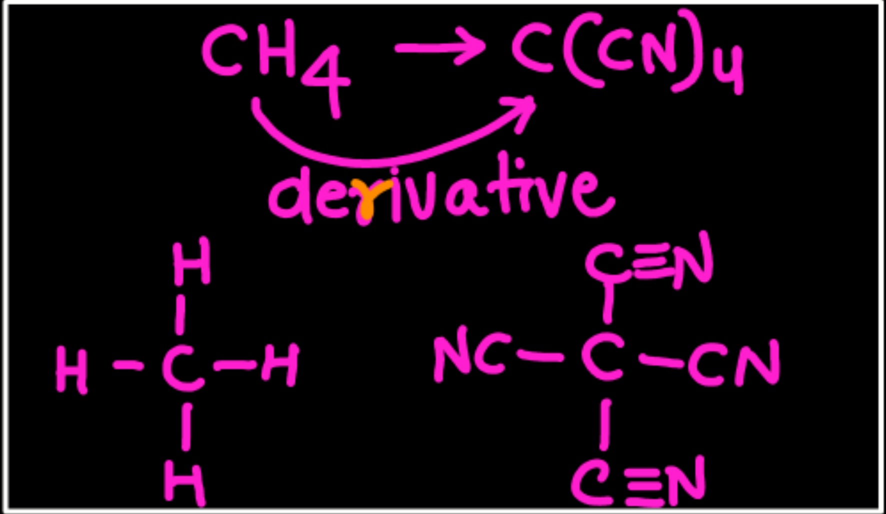
G15 → nitrogen family Ve = 5

G16 → oxygen family Ve = 6

(iv) 

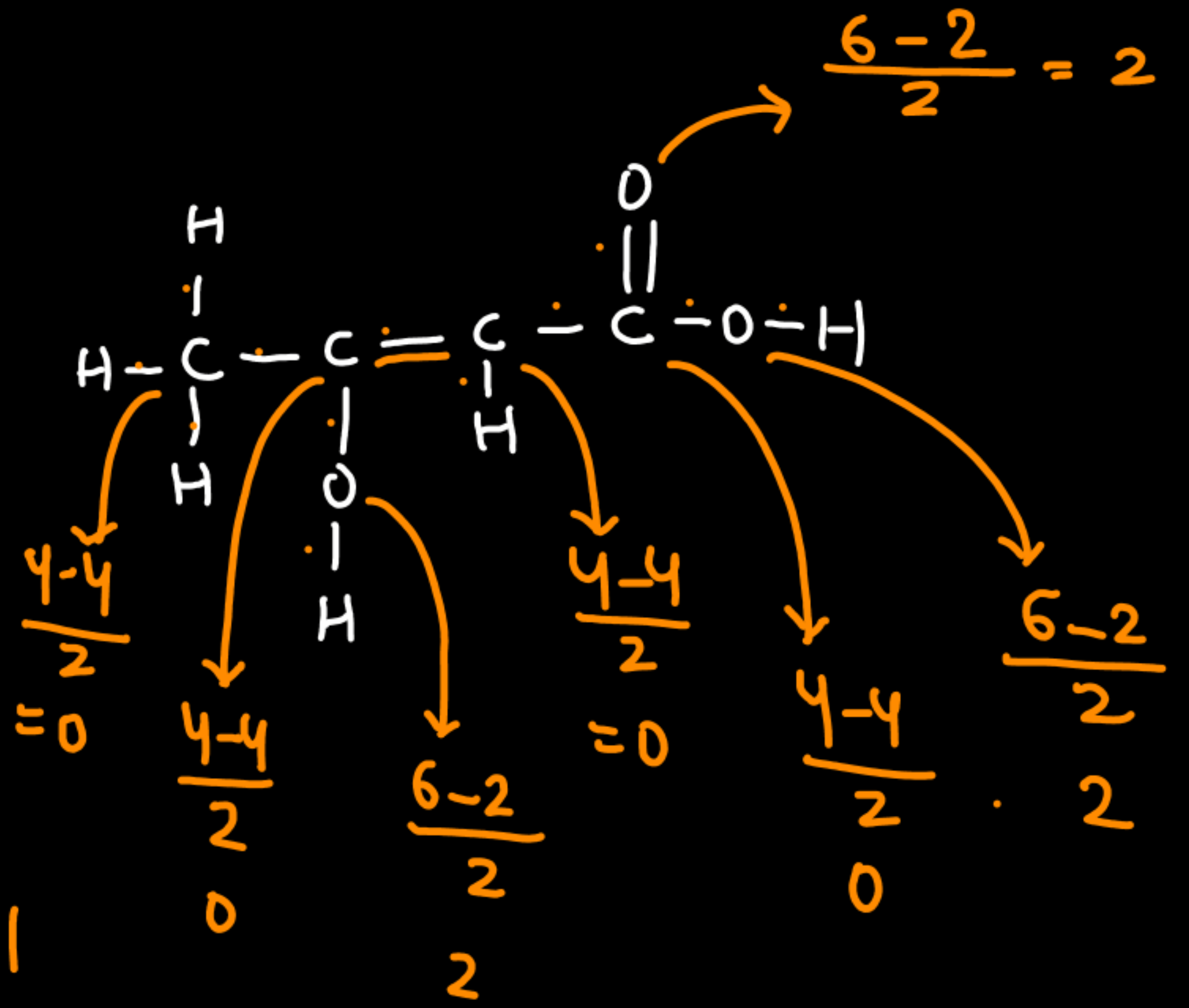


16σ
4π
0 lp



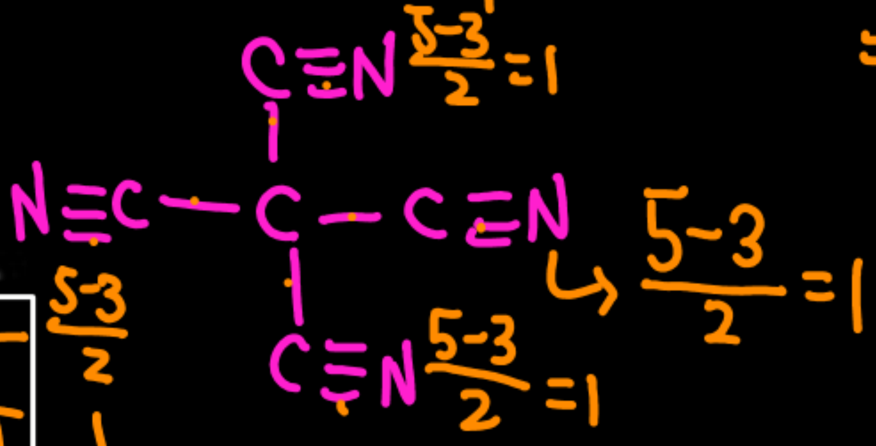
(v) $CH_3 - C(OH) = CH - C(=O) - OH$

12σ
2π
6 lp



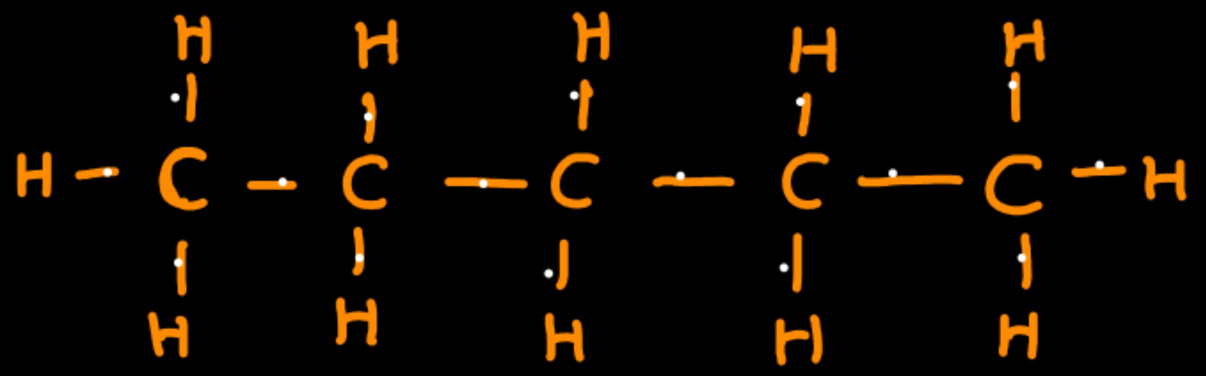
neet PYQ

(vi) $C(CN)_4$



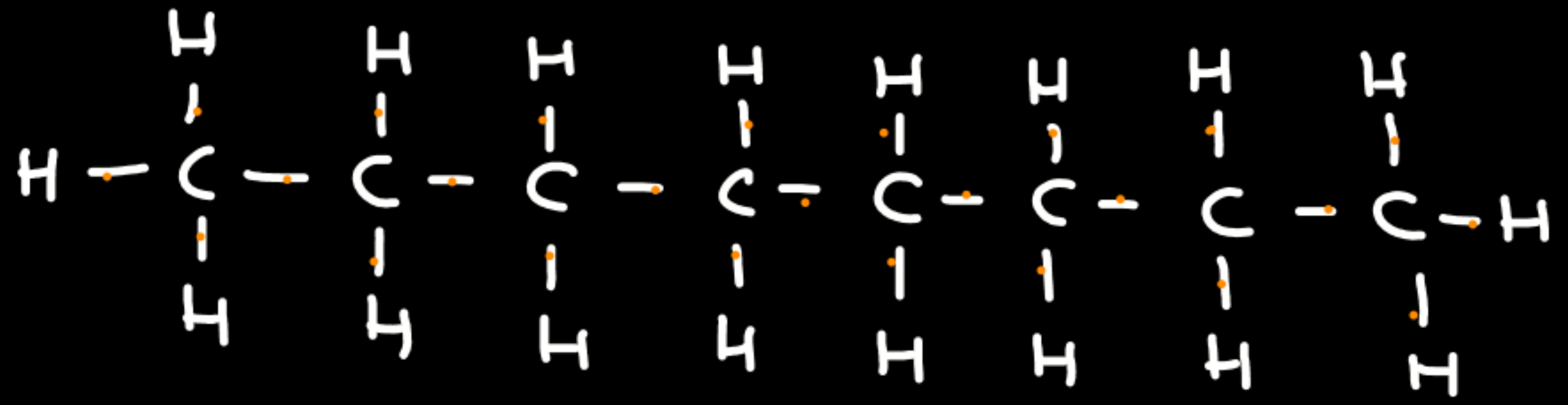
8σ
8π
4 lp

(vii) C_5H_{12}



16σ
0π
0lp

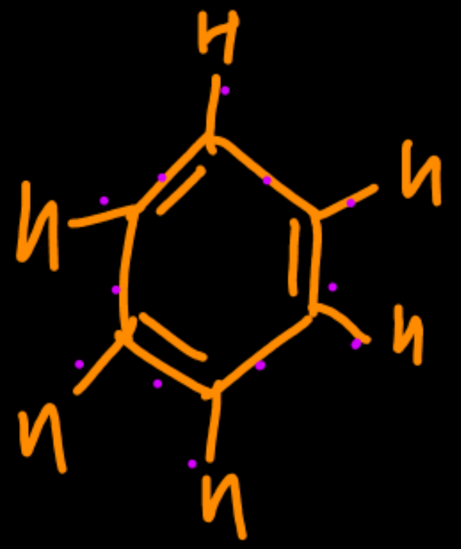
(viii) C_8H_{18}



25σ
0π
0lp

(ix)



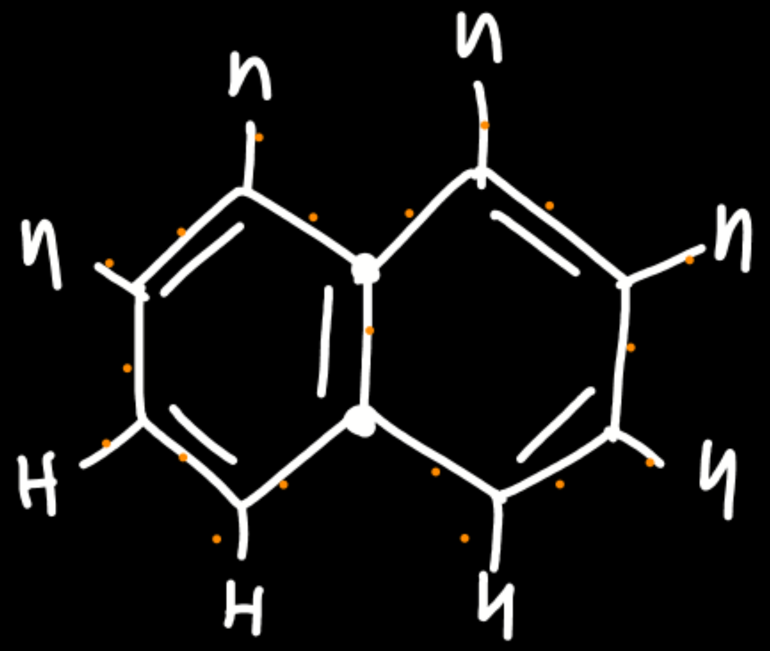


12σ
3π
0lp

neet PYQ

(x)



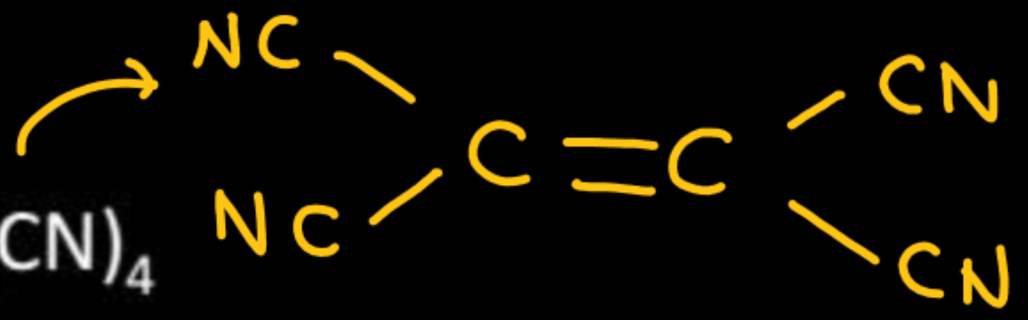


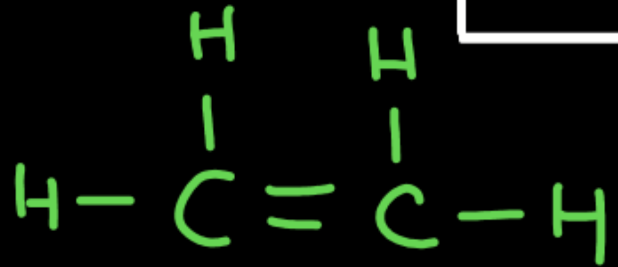
19σ
5π
0 lp

lonepair = $\frac{ve^- - bond}{2}$

neet PYQ

(xi) $C_2(CN)_4$



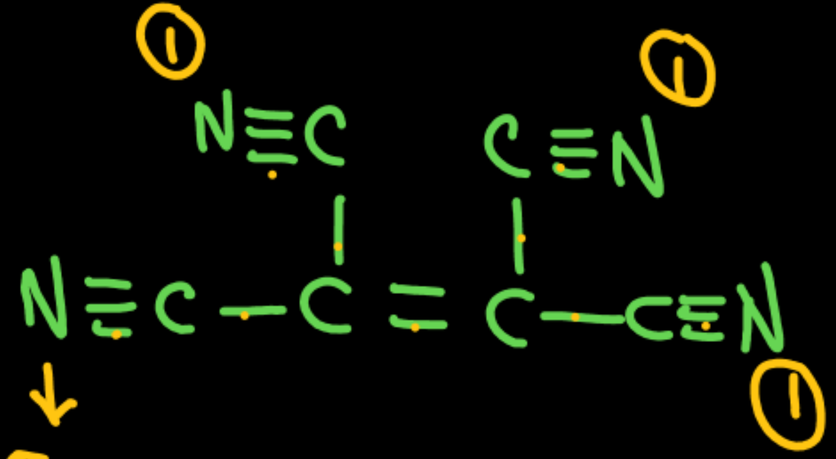


What is sum of σ bond, π bond, lp

$CH_4 \longrightarrow C(CN)_4$

$C_2H_4 \longrightarrow C_2(CN)_4$

(A) 20
(B) 21
(C) 22 ✓
(D) 23



$\frac{5-3}{2} = \frac{2}{2} = 1$

1

9σ
9π
4lp

Hybridization

σ bond + lone pair → Steric no

→ Steric num ↓ σ bond + lp

Steric num	Hybridization
2	sp
3	sp^2
4	sp^3
5	sp^3d
6	sp^3d^2

Jadu

–C– (4 single)	4σ	sp^3
–C= (1 double)	3σ	sp^2
–C≡ (1 triple / 2 double)	2σ	sp
=C= (2 double)	2σ	sp

Steric no	Orbitals	Hybridization	Angle	Shape
2	$s + p_{x/y/z}$	2 (sp)	180°	Linear
3	$s + p_x + p_z$ $s + p_x + p_y$ $s + p_y + p_z$	3 (sp^2)	120°	Trigonal planar
4	$s + p_x + p_y + p_z$	4 (sp^3)	109.5°	Tetrahedral
5	$s + p_x + p_y + p_z + d_{z^2}$	5 (sp^3d)	120°, 90°	Trigonal bipyramidal (TBP)
6	$s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2}$	6 (sp^3d^2)	90°	Octahedral

Que which d orbital is used in sp^3d hybridization –

1. d_{xy}
2. d_{yz}
3. d_{z^2} ✓
4. $d_{x^2-y^2}$

which pair of d orbital is used in sp^3d^2 hybridzⁿ

(A) d_{xy} d_{yz}

(B) $d_{x^2-y^2}$ d_{z^2} ✓

(C) $d_{x^2-y^2}$ d_{xy}

(d) All of above

QUESTION:- Which of the following represent the given mode of hybridization $sp^2 - sp^2 - sp$ from left to right :

(A) $H_2C = CH - C \equiv CH$

(B) $HC \equiv C - C \equiv CH$

(C) $H_2C = CH - CH = CH_2$

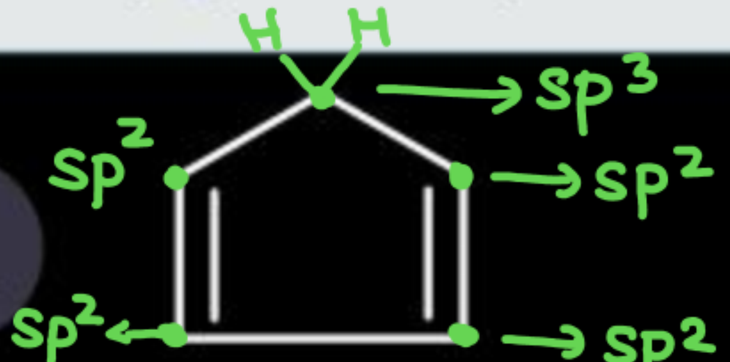
(D) $H_2C = C = C = CH_2$

4 single → sp^3

1 double → sp^2

1 triple / 2 double → sp

QUESTION:- **Which of the following compound has only one type of hybridized carbon atom?**

A 

B 

C 

D All of these

Hybridization → Steric num → σ bond + lp

QUESTION:- Find hybridization of each carbon atom in the given structure :

A $\overset{sp}{CH} \equiv \overset{sp}{C} - \overset{sp^2}{CH} = \overset{sp^2}{CH} - \overset{sp^3}{CH_3}$

B $\underset{sp}{CH} \equiv \underset{sp}{C} - \underset{sp^3}{CH_2} - \underset{sp^3}{CH_2} - \underset{sp^2}{CH} = \underset{sp^2}{CH_2}$

C $\underset{sp^3}{CH_3} - \underset{sp^2}{CH} = \underset{sp^2}{CH} - \underset{sp^3}{CH_2} - \underset{sp^2}{C}(=O) - \underset{sp^3}{CH_3}$

lp $= \frac{6-2}{2} = 2$

Steric no = σ + lp = 1 + 2 = 3 → sp^2

D $\underset{sp^3}{CH_3} - \underset{sp^2}{C}(=O) - \underset{sp^3}{CH_2} - \underset{sp^2}{C}(=O) - OH$

lp $= \frac{6-2}{2} = 2$

σ + lp: 1 + 2, 3 → sp^2

σ + lp = 1 + 2 = 3 = sp^2

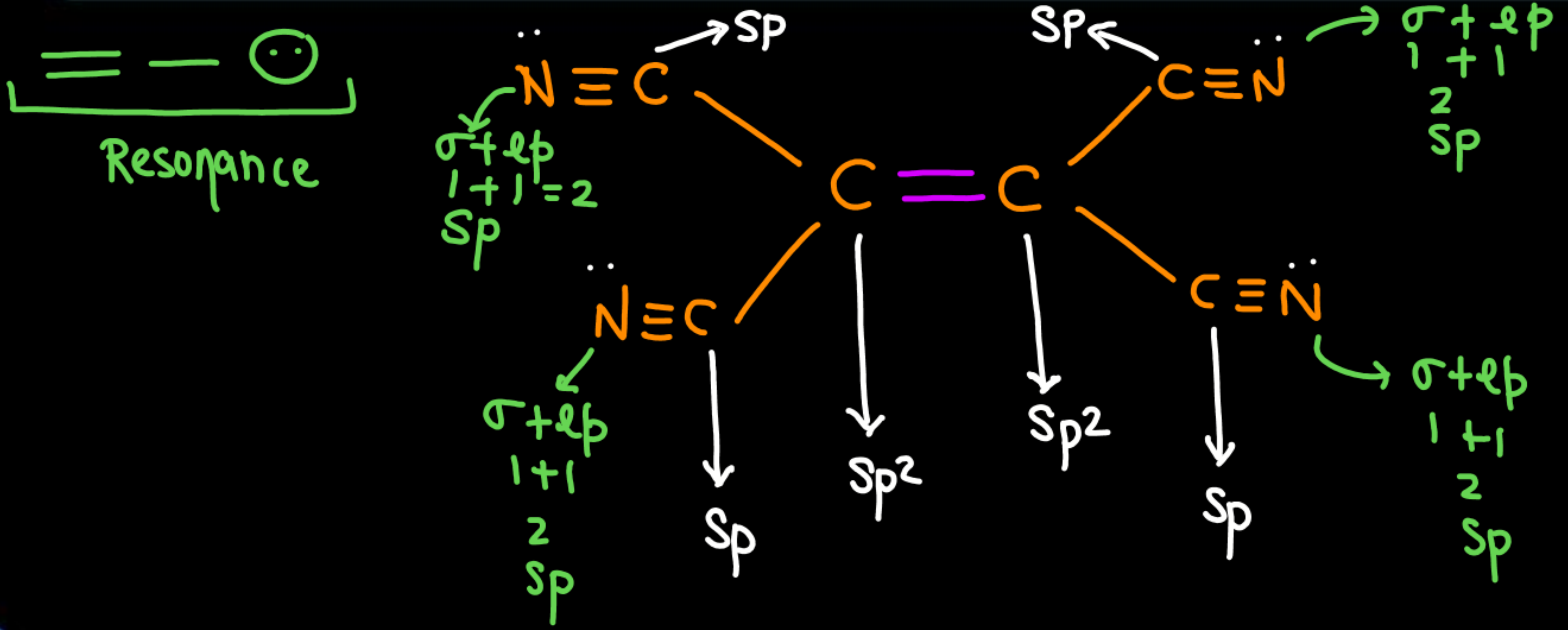
Steric no = σ + lp = 2 + 1 = 3 → sp^2

note → If lonepair is in Resonance then that lonepair is not counted in hybridization.

→ bcoz that lonepair makes pi bond & Pi bond has no role in Hybridization.

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QUESTION:- Calculate hybridization of each atom in $C_2(CN)_4$



QUESTION:- $CH_3 - CH_2 - \overset{\overset{:\ddot{O}:}{||}}{C} - CH = CH - \ddot{N}H_2$

$lp = \frac{ve - bond}{2} = \frac{6-2}{2} = \frac{4}{2} = 2$

Steric no $= \sigma + lp = 1 + 2 = 3 = sp^2$ ✓

$lp = \frac{ve - bond}{2} = \frac{5-3}{2} = \frac{2}{2} = 1$

CH_3	CH_2	C	CH	CH	NH_2
sp^3	sp^3	sp^2	sp^2	sp^2	Steric Num

Steric Num $= \sigma bond + lp$
$= 3 + 1$
$= 4$
~~$= sp^3$~~

$= - \ddot{\ }$ Resonance

Steric num $= \sigma bond + lp$
$= 3 + 0$
$= 3$
$= sp^2$ ✓

= – Ö

QUESTION:- $CH_2 = CH - CH_2 - \ddot{N}H_2$

CH_2 → sp^2

CH → sp^2

CH_2 → sp^3

$\ddot{N}H_2$ → Steric no = σ + lp
= 3 + 1
= 4
= sp^3

Neet PYQ

QUESTION:- What is the hybridization of carbon in acetonitrile ?

A) sp^3, sp

B) sp^3, sp^3

C) sp, sp

D) sp^2, sp

Acet → 2 carbon

nitrile → C≡N

<u>Acetonitrile</u>

$CH_3 — C \equiv \ddot{N}$

CH_3 → sp^3

C → sp

N → σ + lp: 1 + 1 = 2 → sp

QUESTION:- What is the hybridization of carbon in allene?

(A) sp^2 sp sp^2 ✓

(B) sp sp^2 sp^2

(C) sp^2 sp^2 sp^2

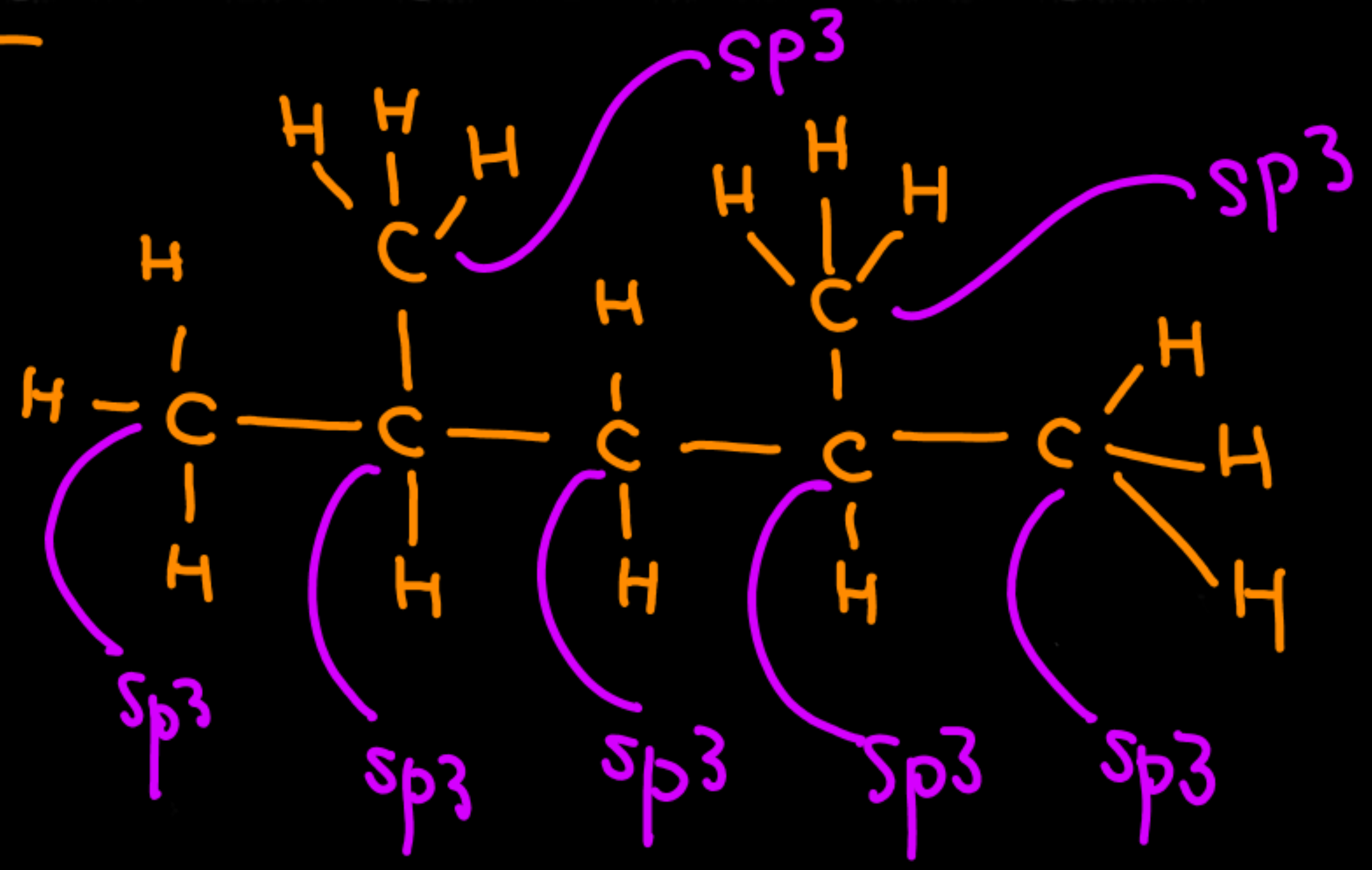
(D) sp sp sp^3

$H_2C = C = CH_2$

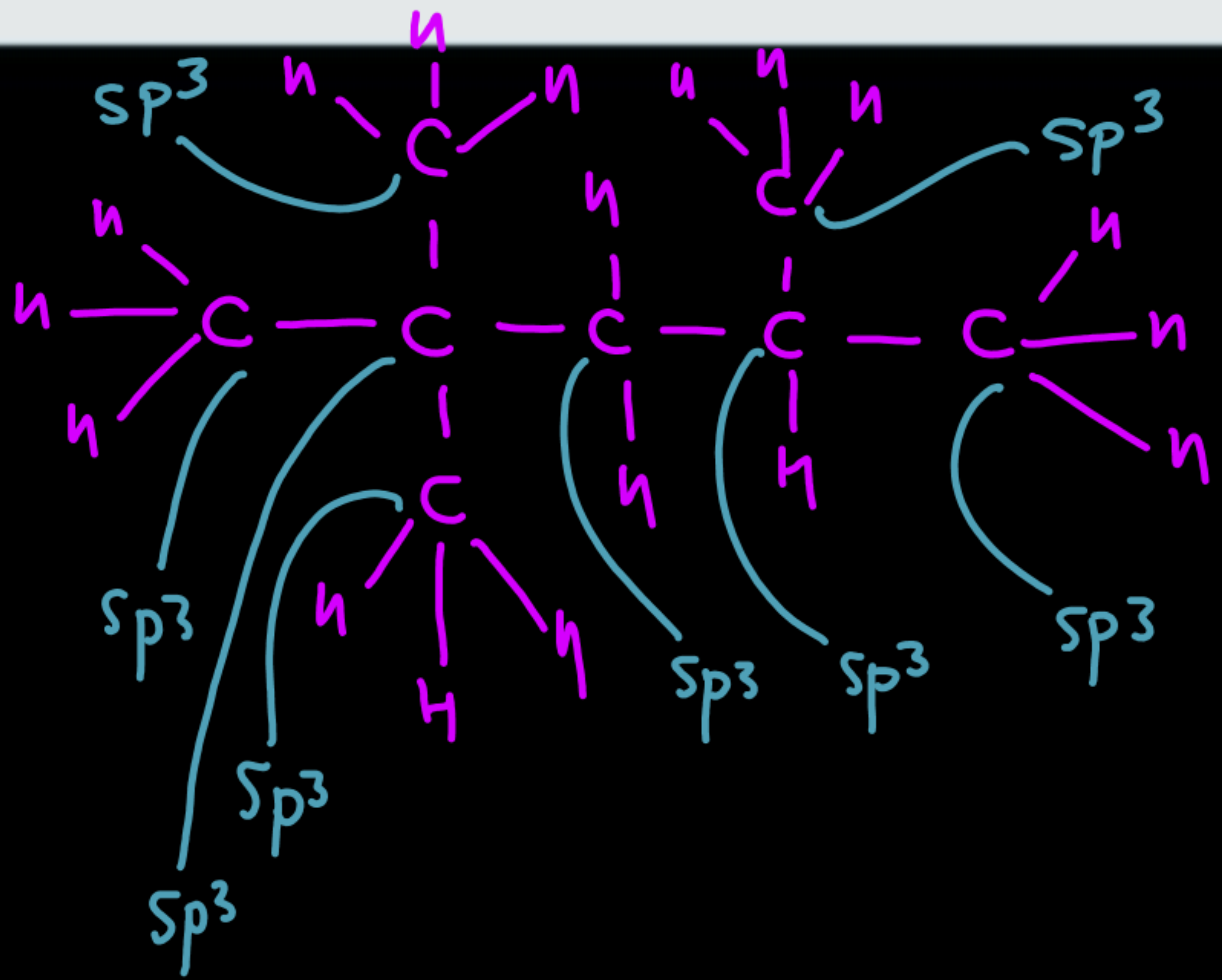
sp^2 sp sp^2

QUESTION:- **Write hybridization of all atoms-**

(i) $CH_3\,CH\,(CH_3)\,CH_2\,CH\,(CH_3)_2$

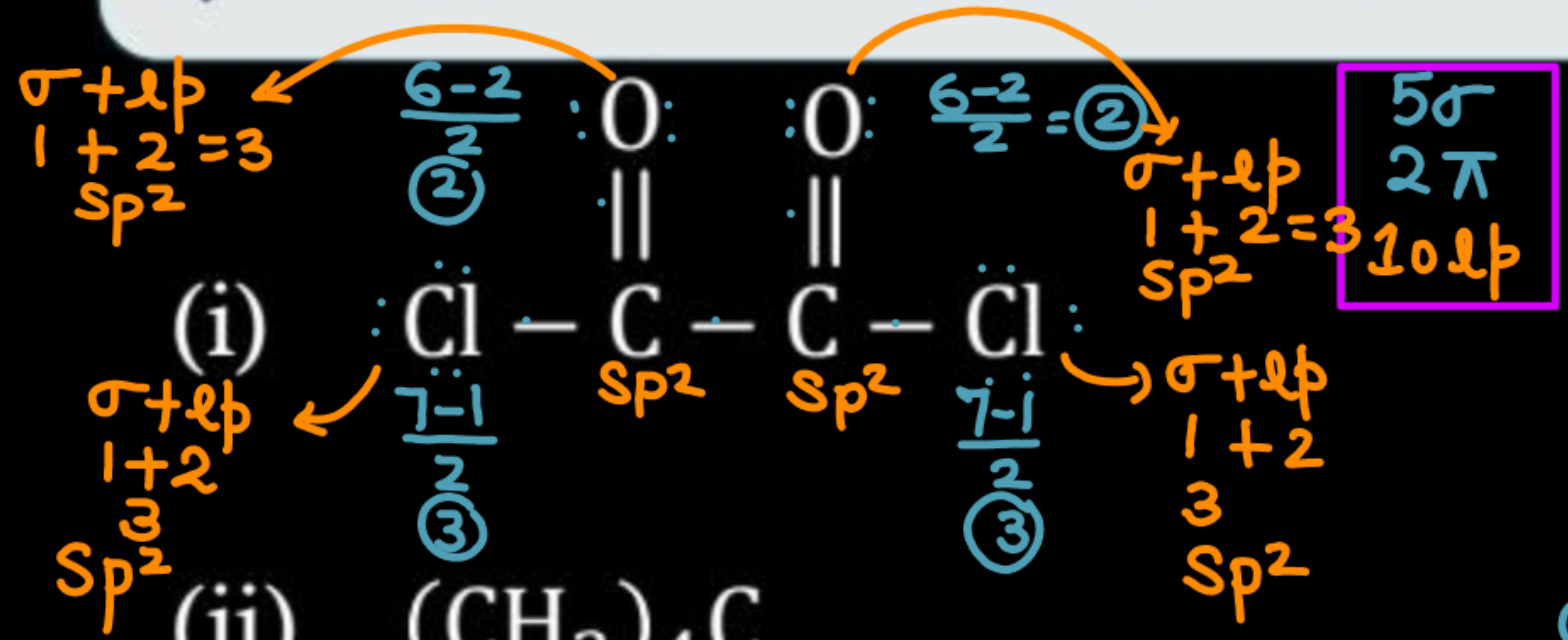


QUESTION:- Write hybridization of all atoms in isooctane

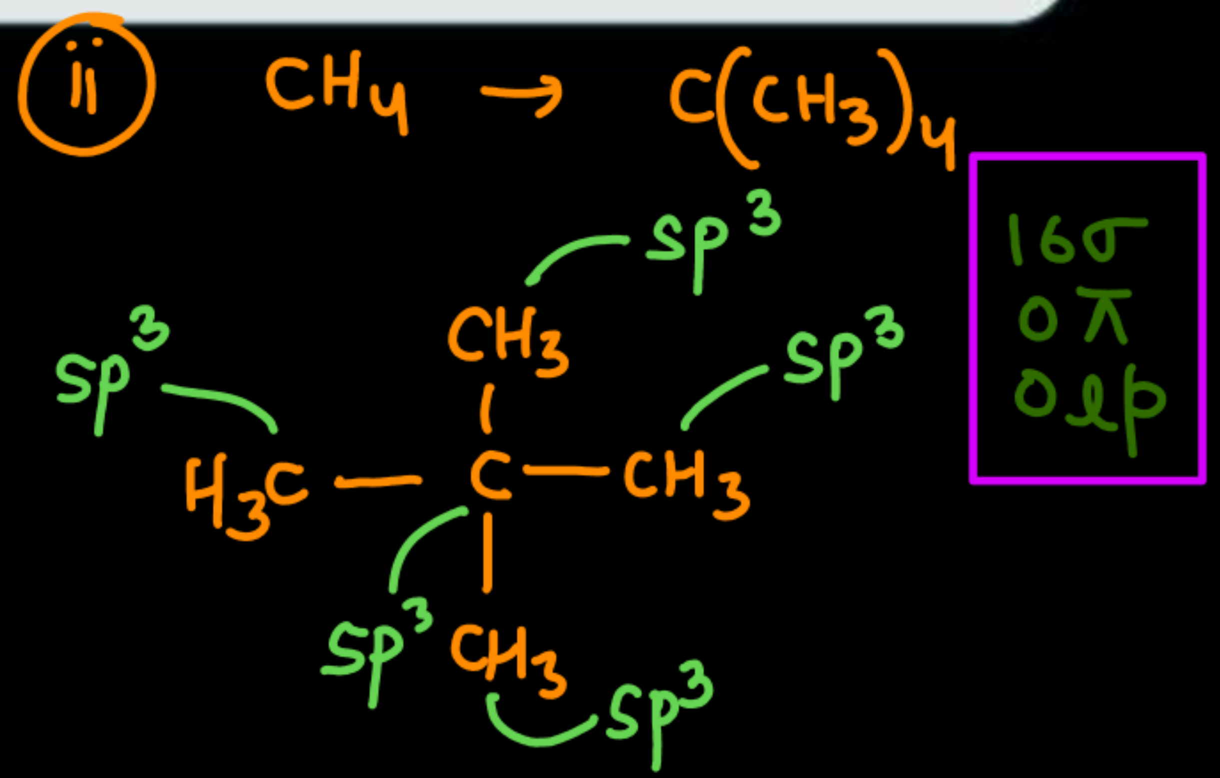


QUESTION:- Calculate σ & π – bond and find out hybridization of each carbon.

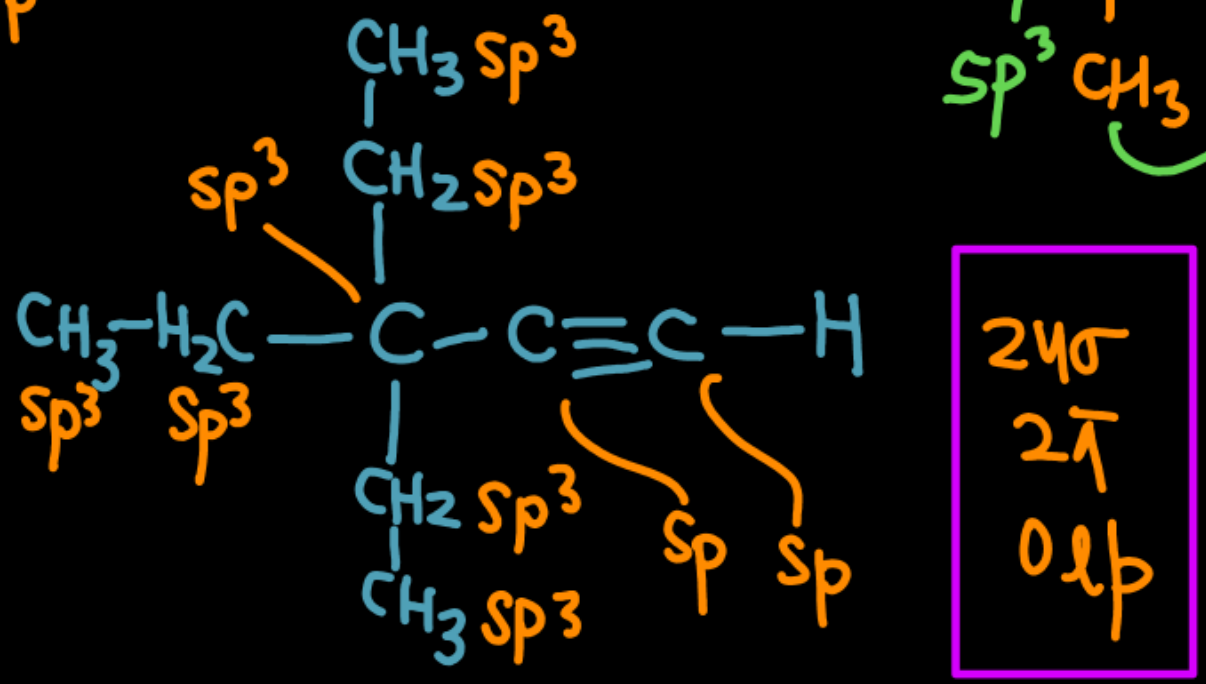
(i)



(ii) $(CH_3)_4C$



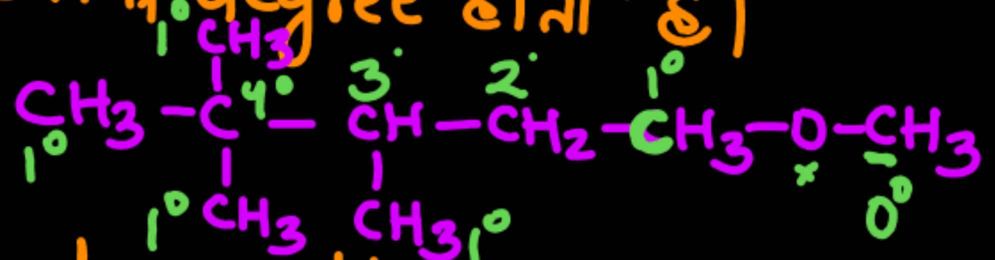
(iii) $(CH_3CH_2)_3CCCH$



Degree of Carbon

एक Carbon कितने other Carbon से bond बना रहा है, वही उसकी degree होती है।

Super primary Carbon (0° degree Carbon) → CH_3-OH (0°),



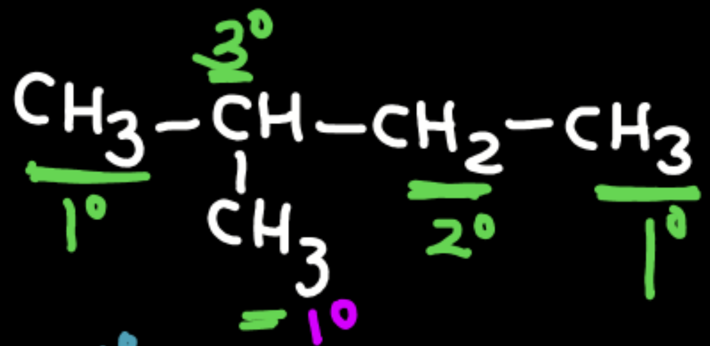
Primary carbon (1° degree Carbon) → Carbon is bonded one other Carbon.

CH_3-CH_3 (1°, 1°)

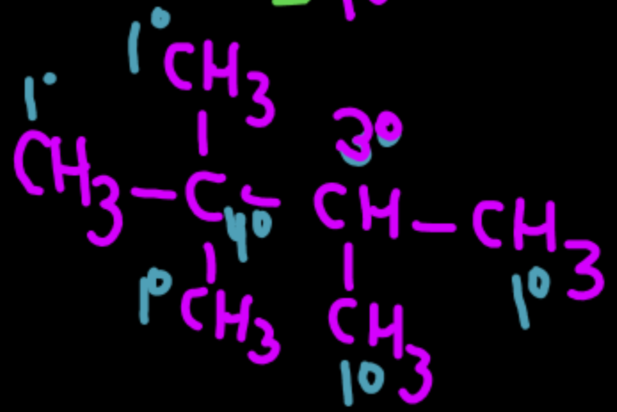
Secondary Carbon (2° degree Carbon) → Carbon is bonded to 2 other Carbon.

$CH_3-CH_2-CH_3$ (1°, 2°, 1°)

Tertiary Carbon (3° degree Carbon) →

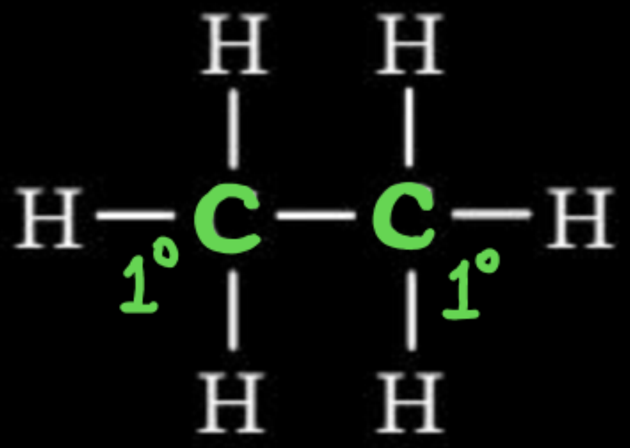


Quatarnary Carbon (4° degree Carbon) →

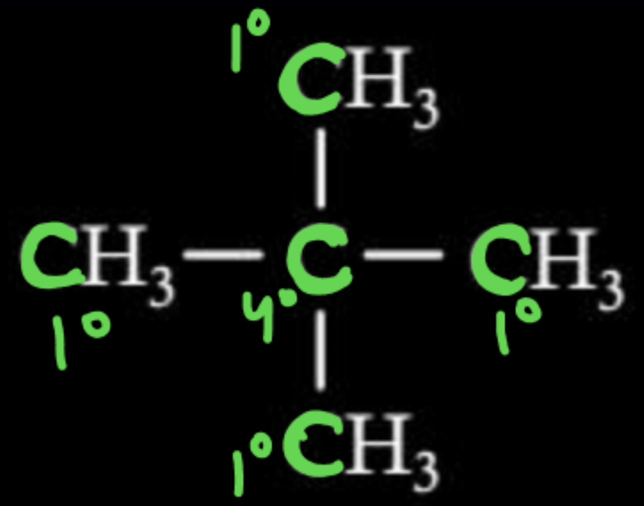


QUESTION:- Find degree of each carbon in the following compound :

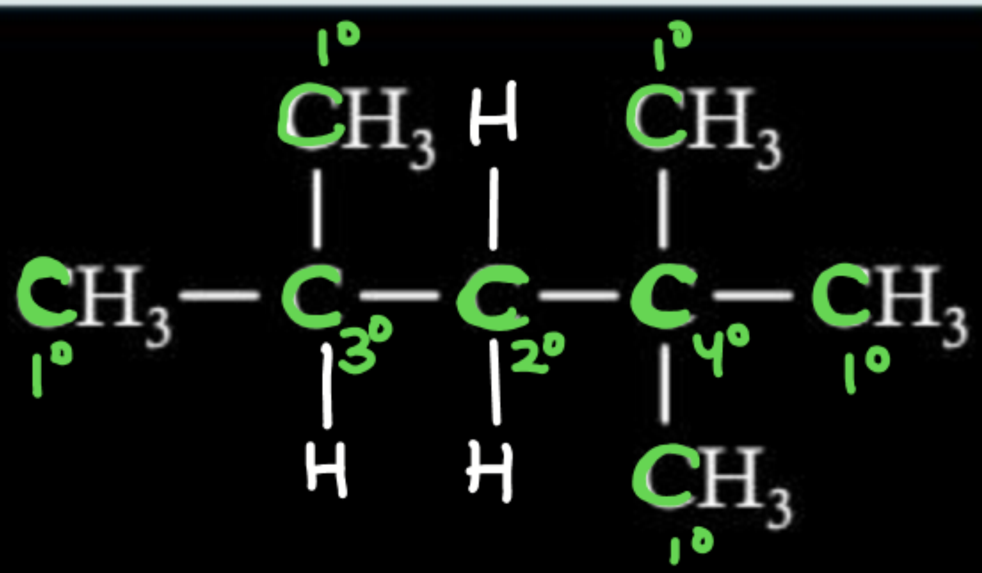
(i)



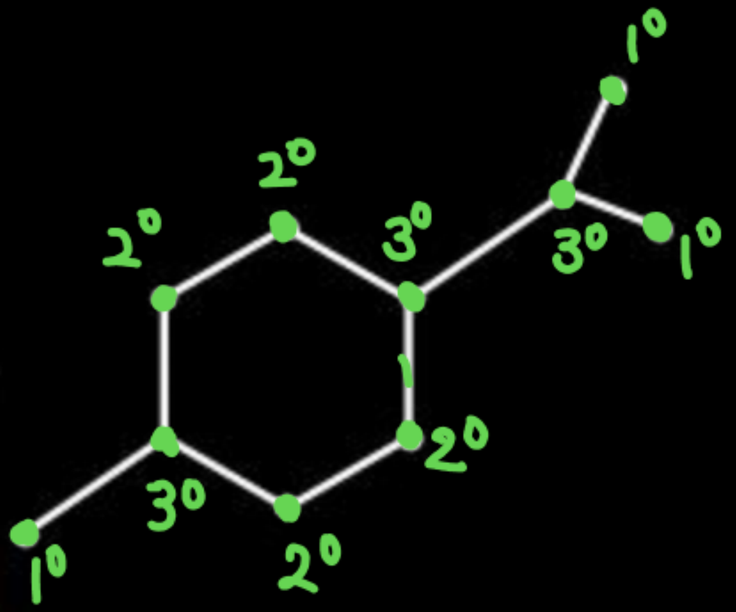
(ii)



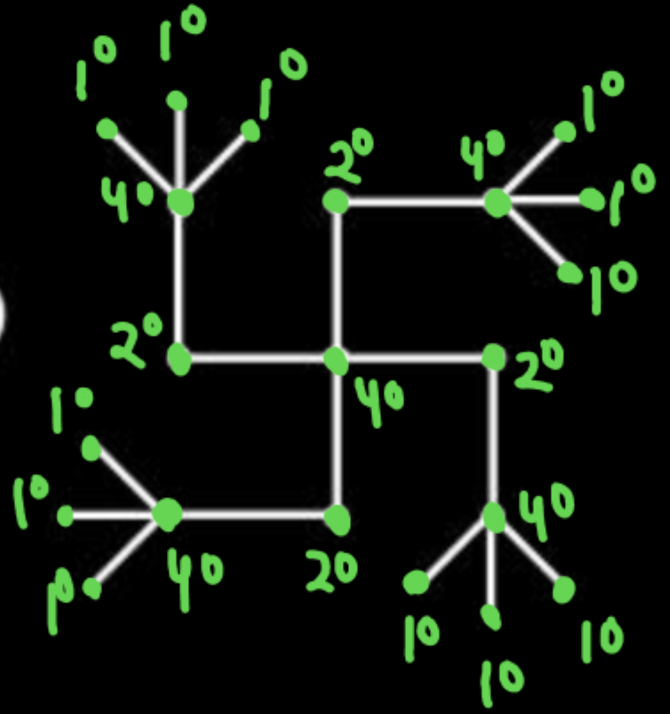
(iii)



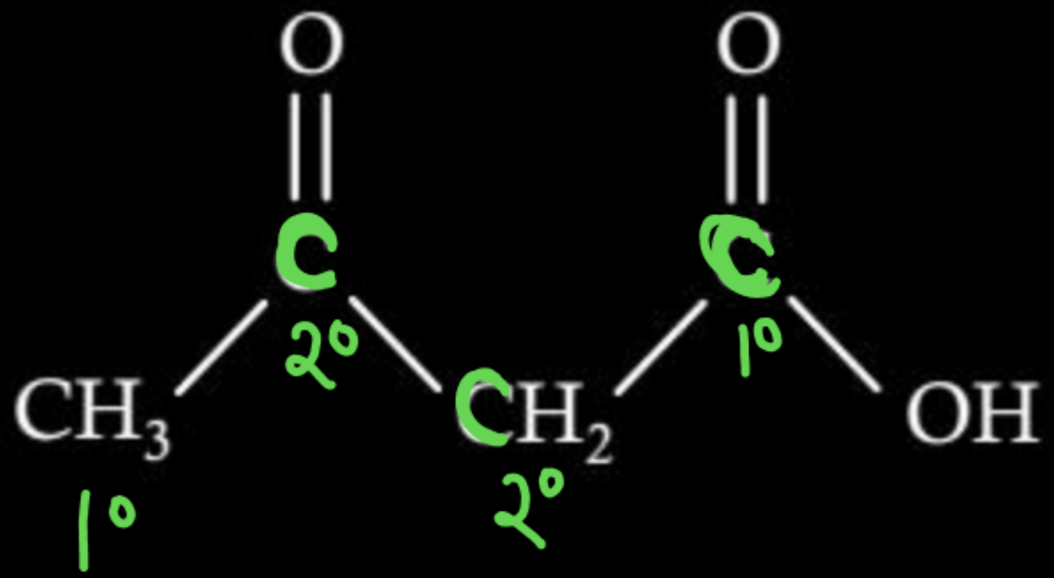
(iv)



(v)

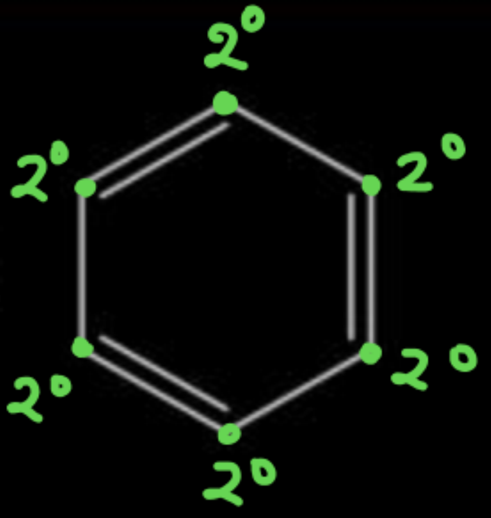


(vi)

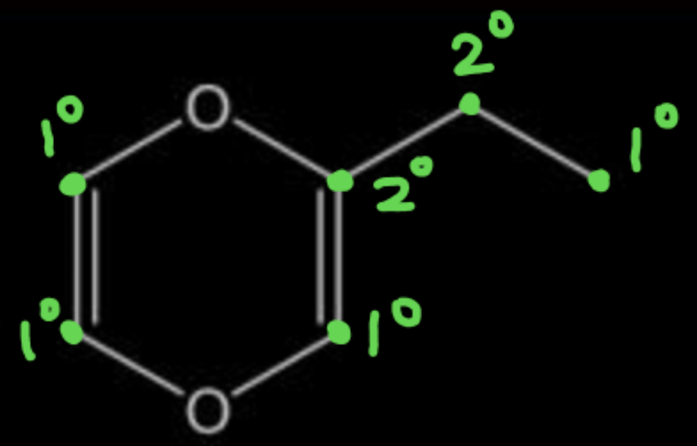


QUESTION:- Find degree of each carbon in the following compound :

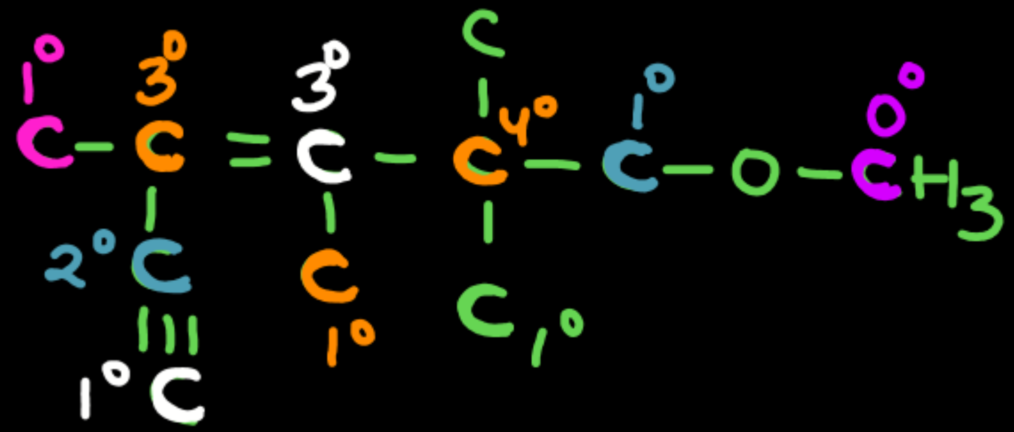
neet
(vii)
PYQ



neet
(viii)
PYQ



(ix)



1° Carbon = 4

2° Carbon = 2

3° Carbon = 0

4° carbon = 0

Degree of Hydrogen

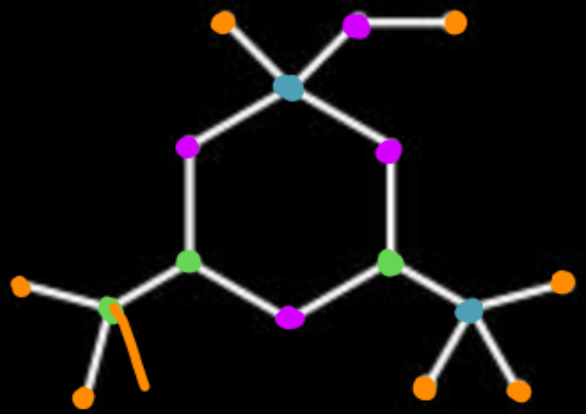
Primary/1° Hydrogen → Hydrogen connected to 1° Carbon/Primary C.

Secondary/2° Hydrogen → " " " 2° Carbon/Secondary C.

Tertiary/3° Hydrogen → " " " 3° Carbon/Tertiary C.

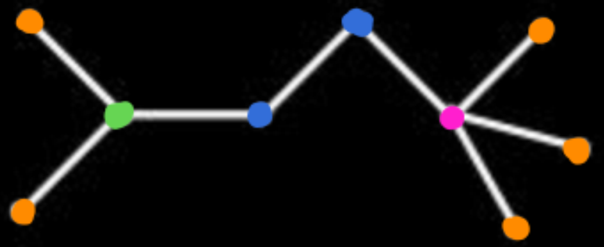
Quatarnary/4° Hydrogen → do not exist.

QUESTION:- Calculate degree of hydrogen in the following compound :



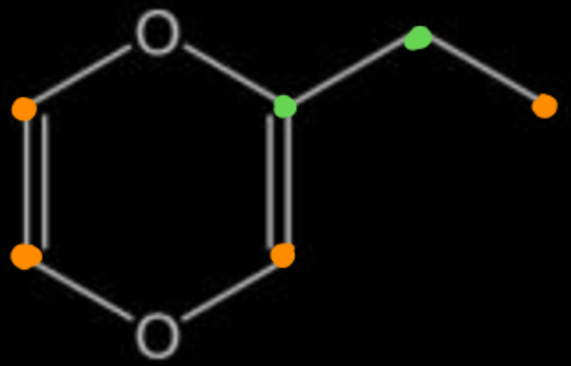
1°C – 7
2°C – 4
3°C – 3
4°C – 2

1°H – 21
2°H – 8
3°H – 3
4°H → X



1°C – 5
2°C – 2
3°C – 1
4°C – 1

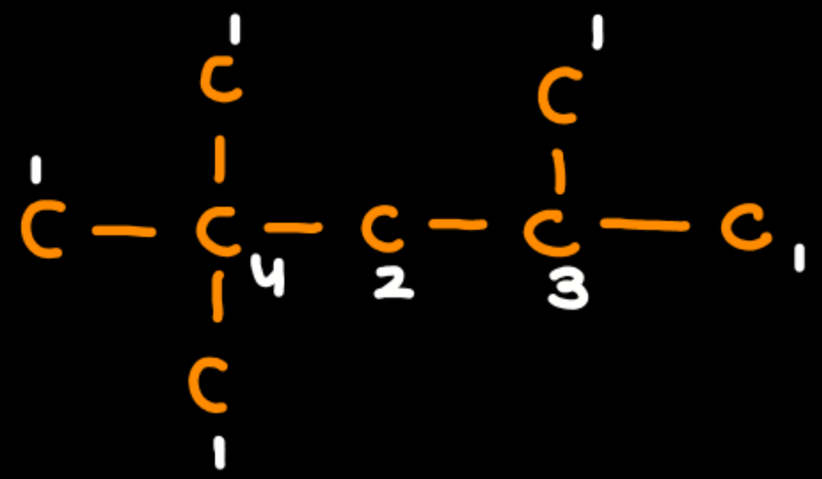
1°H – 15
2°H – 4
3°H – 1
4°H – X



1°C – 4
2°C – 2
3°C – X
4°C – X

1°H – 6
2°H – 2

QUESTION:- Write all degree of Carbon & Hydrogen in isooctane-



1° C – 5	1° H = 15
2° C – 1	2° H = 2
3° C – 1	3° H = 1
4° C – 1	4° H = X

acetonitrile

$H_3C - C \equiv N$
(1°) (1°)

1° C = 2	1° H = 3
2° C – X	2° H = X
3° C – X	3° H = X
4° C – X	4° H = X

allene

$CH_2 = C = CH_2$
(1°) (2°) (1°)

1° C = 2	1° H = 4
2° C = 1	2° H = 0
3° C = X	3° H = X
4° C = X	4° H = X

Degree of Alcohol & Halogen

Primary alcohol (1°) → OH is connected to 1° carbon.

Secondary alcohol (2°) → OH is connected to 2° carbon.

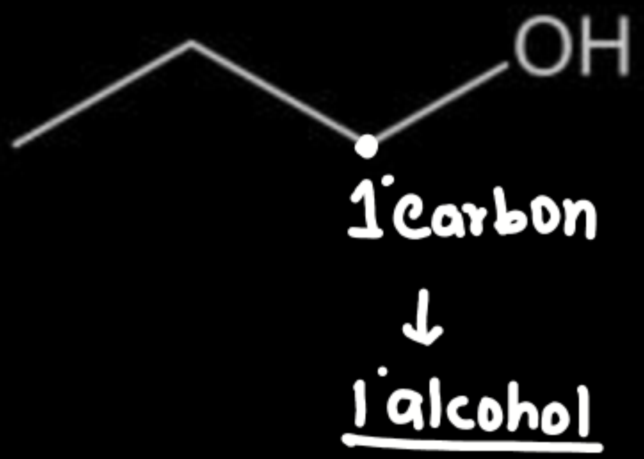
Tertiary alcohol (3°) → OH is connected to 3° carbon.

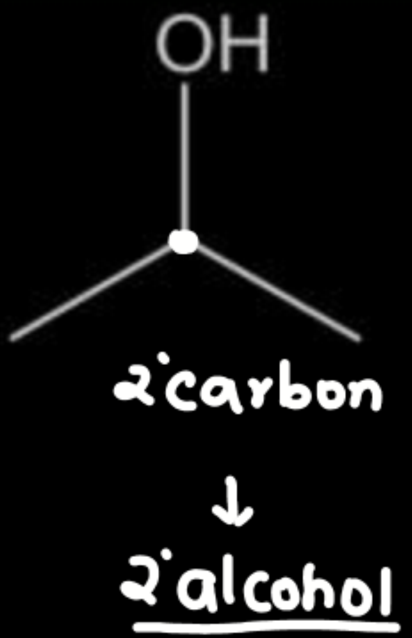
Primary Halogen (1°) → X is connected to 1° carbon.

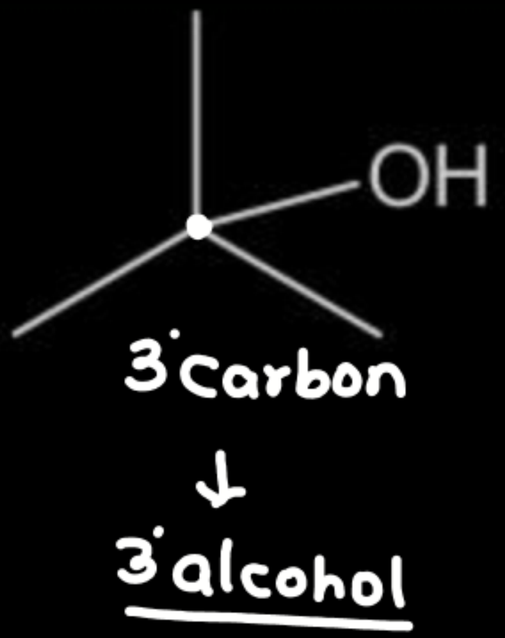
Secondary " (2°) → X " " " 2° " .

Tertiary " (3°) → X " " " 3° " .

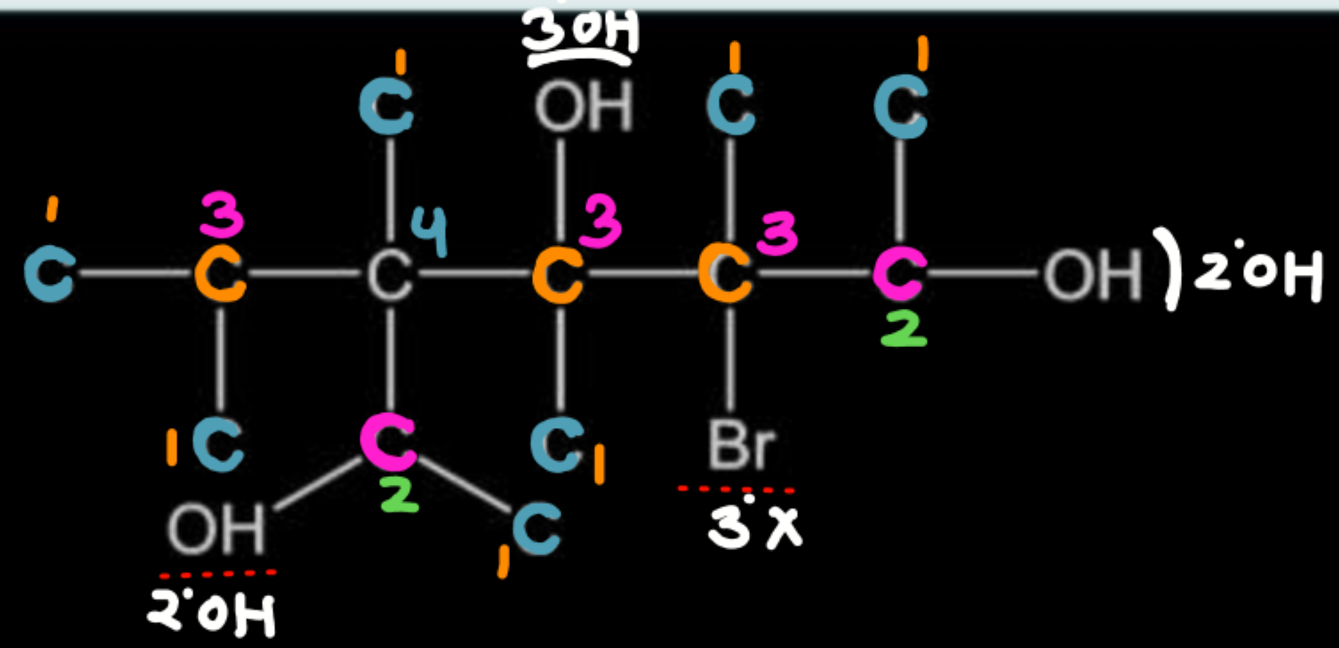
QUESTION:- Write degree of alcohol in following compound-





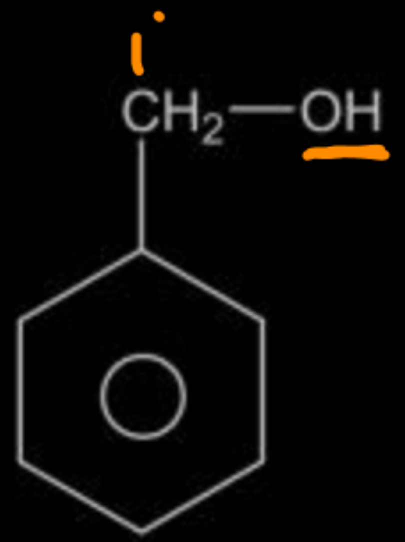


QUESTION:- Write degree of alcohol & Halogen in following compound-

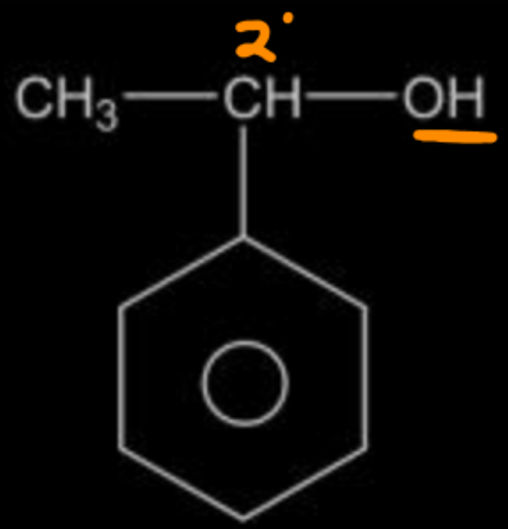


1°C-7	1°H-21	1°OH-x	1°X-x
2°C-2	2°H-2	2°OH-2	2°X-x
3°C-3	3°H-1	3°OH-1	3°X-1
4°C-1			

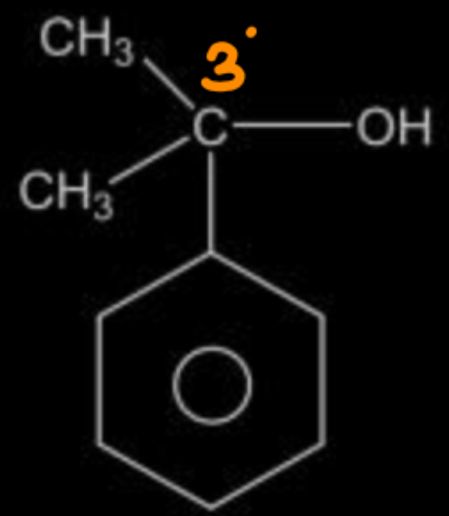
QUESTION:- Write degree of alcohol in following compound-



1° alcohol



2° alcohol



3° alcohol



~~2° alcohol~~

Phenol

↓

degree not defined

note → alcohol & phenol are diff comp.

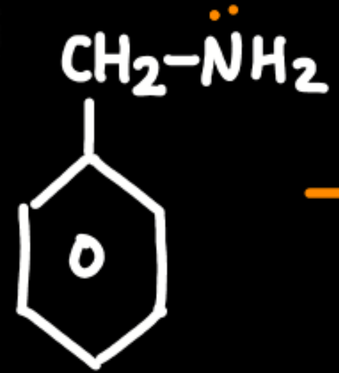
Degree of Amine

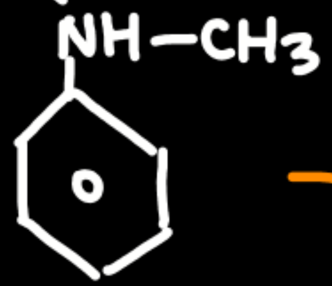
NH_3 → ammonia
└→ derivative

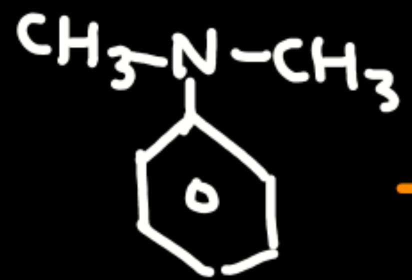
note → alcohol & phenol → diff
Amine & Aniline → diff

N is bonded to 1C	$R—\ddot{N}H_2$	→ 1° amine
N is bonded to 2C	$R—\ddot{N}H—R$	→ 2° amine
N is bonded to 3C	$R—\ddot{N}(R)—R$	→ 3° amine
	$R—N(R)(R)—R$	→ 4°/Quatarnary ammonium Salt

Q


→ 1° amine

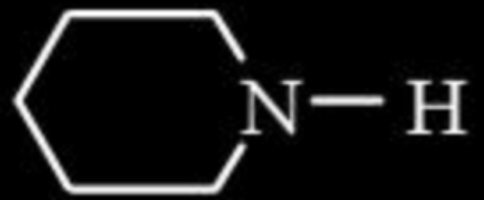

→ 2° amine


→ 3° amine

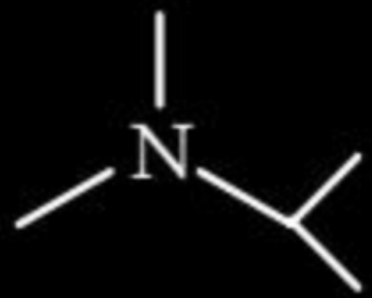

→ 4° ammonium Salt


→ Aniline (degree not defined)

QUESTION:- **Indicate the following as 1°, 2° and 3° amines.**



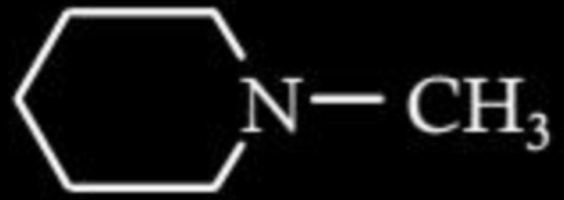
2°amine



3°amine



2°amine

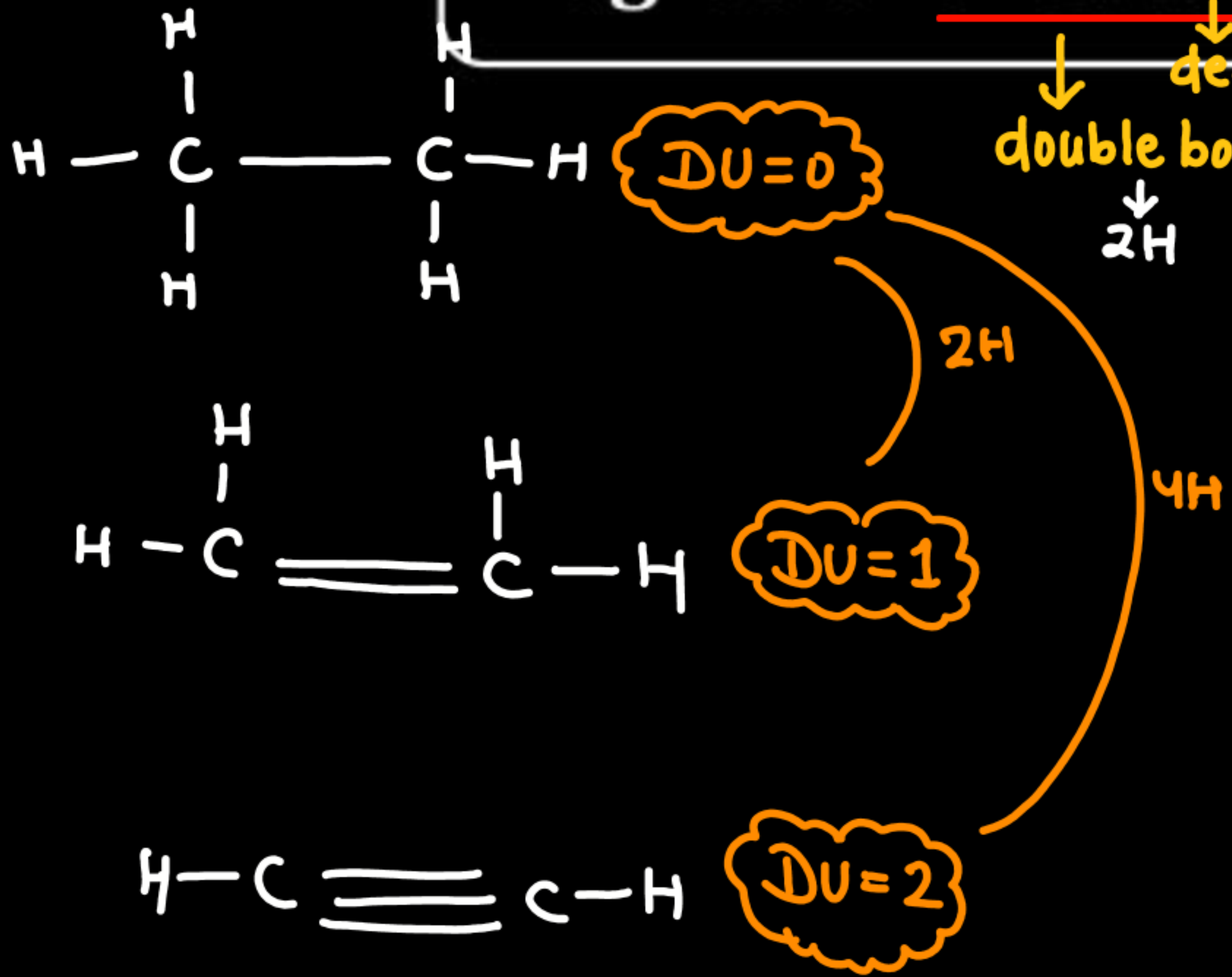


3°amine

Degree of Unsaturation (DU)

↓ deficiency of Hydrogen

double bond , triple bond , Ring
↓ 2H ↓ 4H ↓ 2H



DU → Degree of Unsaturation
DBE → Double bond equivalent
IHD → Index of Hydrogen deficiency

DU/DBE/IHD is deficiency of pair of Hydrogen.

or

1 double bond → DU=1
1 triple bond → DU=2
1 Ring → DU=1

Calculation of DU/ DBE/ IHD

Formula Given

$$DU = (C+1) - \left(\frac{H+X-N}{2}\right)$$

C = no of Carbon
H = " " Hydrogen
I/Br/Cl/F ← X = " " Halogen family element
Sb/As/P/N ← N = " " Nitrogen family element

Str given

DU = π bond + Ring

QUESTION:- **Calculate double bond equivalent (DBE) of following compounds :**

(i) $C_{10}H_{10}$

$(C+1)-\left(\frac{H+X-N}{2}\right)$

$(11)-\left(\frac{10+0-0}{2}\right)$

$11-\left(\frac{10}{2}\right)$

6

(ii) C_4H_{10}

$(C+1)-\left(\frac{H+X-N}{2}\right)$

$(4+1)-\left(\frac{10+0-0}{2}\right)$

$5-\left(\frac{10}{2}\right)=0$

(iii) C_2H_2

$(C+1)-\left(\frac{H+X-N}{2}\right)$

$3-\left(\frac{2}{2}\right)$

2

(iv) C_3H_3F

$(4)-\left(\frac{3+1-0}{2}\right)=4-2=2$

all are isotope
all are equal
H=D=T

(v) $C_3D_2T_2FCl$

$(4)-\left(\frac{4+2-0}{2}\right)$

$4-\frac{6}{2}$

$4-3$

1

(vi) $C_6HDTF_2ClBr_2$

$7-\left(\frac{3+5-0}{2}\right)$

$7-\frac{8}{2}$

3

QUESTION:- Calculate double bond equivalent (DBE) of following compounds :

(vii) C_3O_2

$$(C+1)-\left(\frac{H+X-N}{2}\right)$$

$$(4)-\left(\frac{0+0+0}{2}\right)$$

$$4$$

(viii) $C_8H_3Cl_3N_2$

$$(9)-\left(\frac{3+3-2}{2}\right)$$

$$9-(2)$$

$$7$$

(ix) $C_2H_6N_2$

$$(3)-\left(\frac{6+0-2}{2}\right)$$

$$3-(2)$$

$$1$$

(x) $C_4H_4O_4$

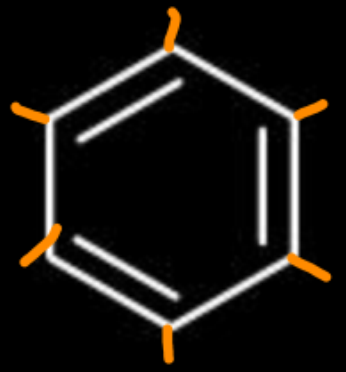
$$(5)-\left(\frac{4+0-0}{2}\right)$$

$$5-(2)$$

$$3$$

QUESTION:- Calculate double bond equivalent (DBE) of following compounds :

(xi)



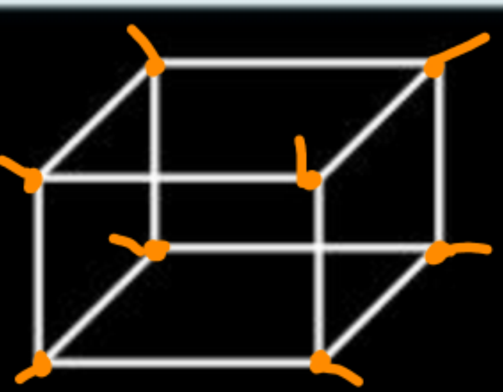
C_6H_6

$7-\left(\frac{6}{2}\right)$

$7-3$

④

(xii)



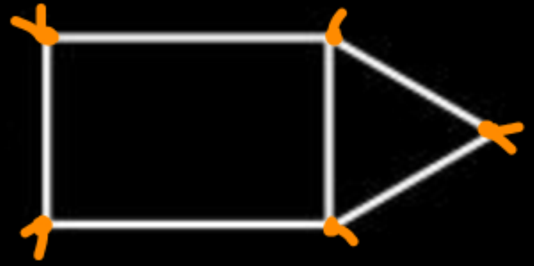
C_8H_8

$9-\left(\frac{8}{2}\right)$

$9-4$

⑤

(xiii)



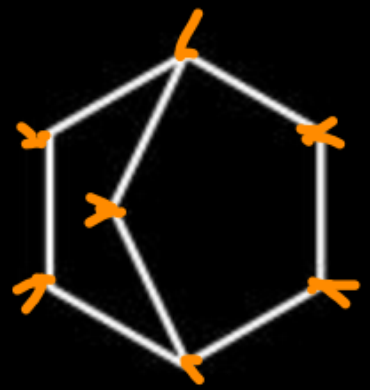
C_5H_8

$6-\left(\frac{8}{2}\right)$

$6-4$

②

(iv)



C_7H_{12}

$8-\left(\frac{12}{2}\right)$

$8-6$

②

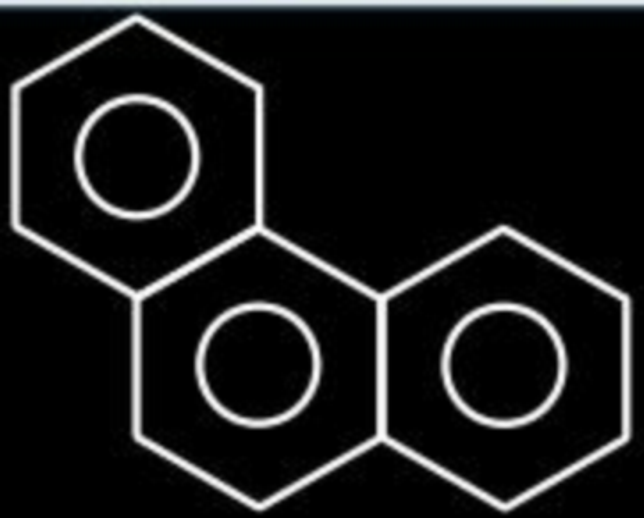
QUESTION:- Calculate double bond equivalent (DBE) of following compounds :

(xii) 

Naphthalene

(xiii) 

Antrancene

(xiv) 

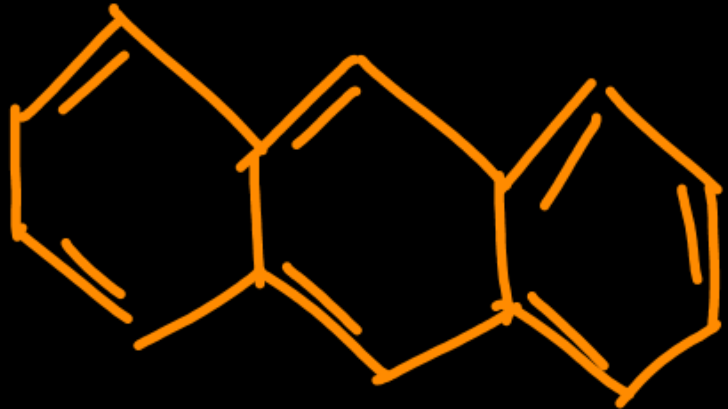
Phenanthacene



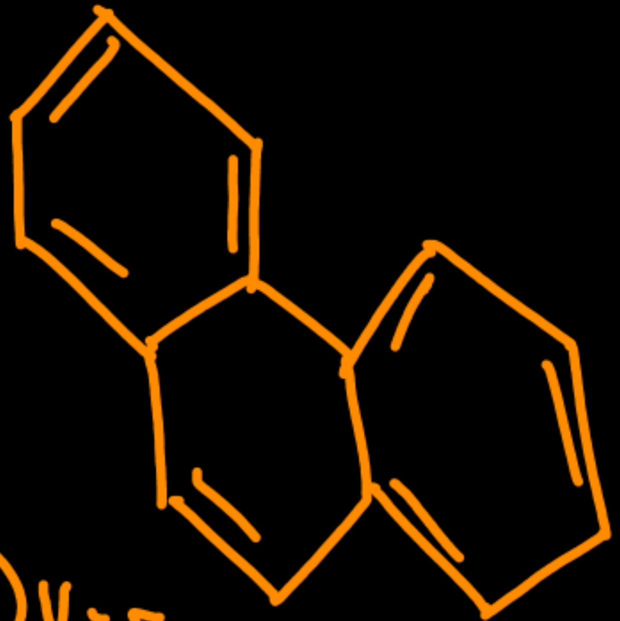
$DU = \pi + R$
$= 3 + 1$
$= 4$



$DU = \pi + R$
$= 5 + 2$
$= 7$



$DU = \pi + R$
$= 7 + 3$
$= 10$



$DU = 7 + 3$
$= 10$

QUESTION:- Which of the following compounds has DBE equal to Benzene?

Neet PYQ

A 

π + R
3 + 1
4

B 

π + R
3 + 1
4



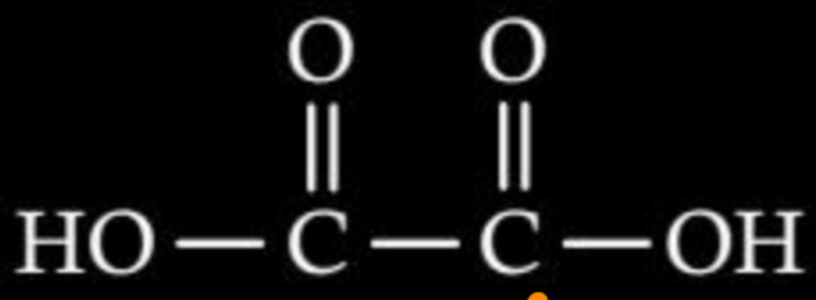
DU = π + R
= 3 + 1
= 4

C 

π + R
3 + 1
4

D All of these ✓

QUESTION:- What is the DBE in the following given structure?

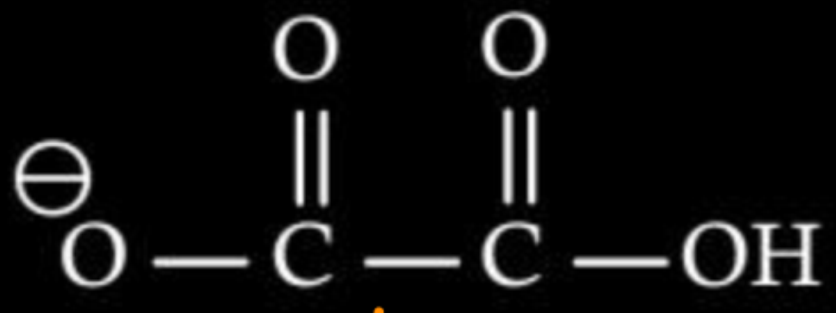


$C_2H_2O_4$

$(3)-\left(\frac{2+0-0}{2}\right)$

$3-1$

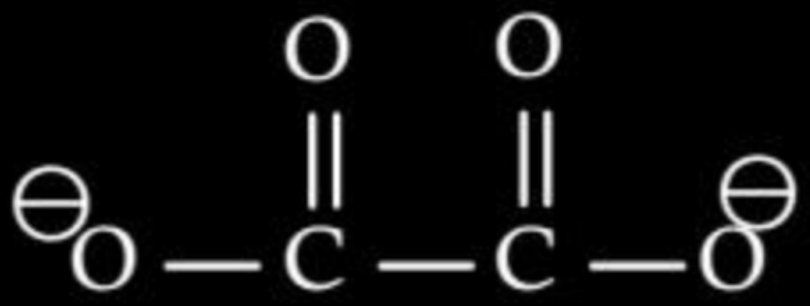
(2)



$C_2HO_4^{\ominus}$

$(3)-\left(\frac{1+0-0}{2}\right)$

(2.5)



$C_2O_4^{-2}$

$(3)-\left(\frac{0+0-0}{2}\right)$

$3-0$

(3)

(A) 2, 3, 4

(B) 2, 3, 5

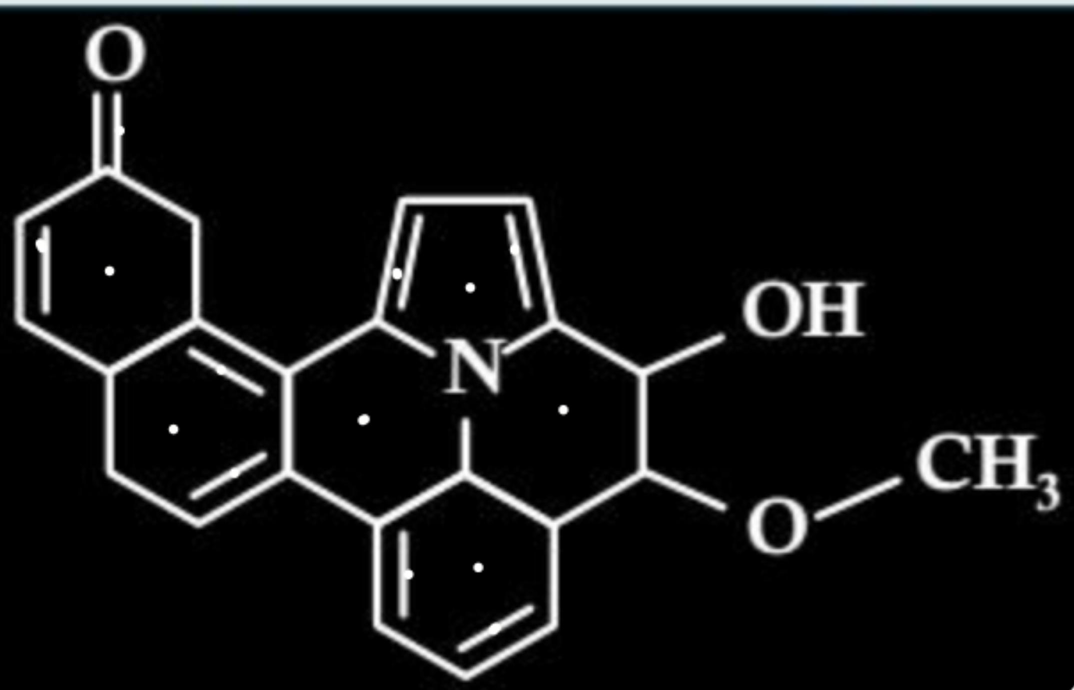
(C) 2, 2.5, 3 ✓

(D) 2, 2.5, 3.5

Note → DU can be +ve,
can be zero,
can be fractional (anion)
DU can never be -ve.

QUESTION:- Find the DBE (Double Bond Equivalent) of the compound?

DU = π + R
= 8 + 6
= 14



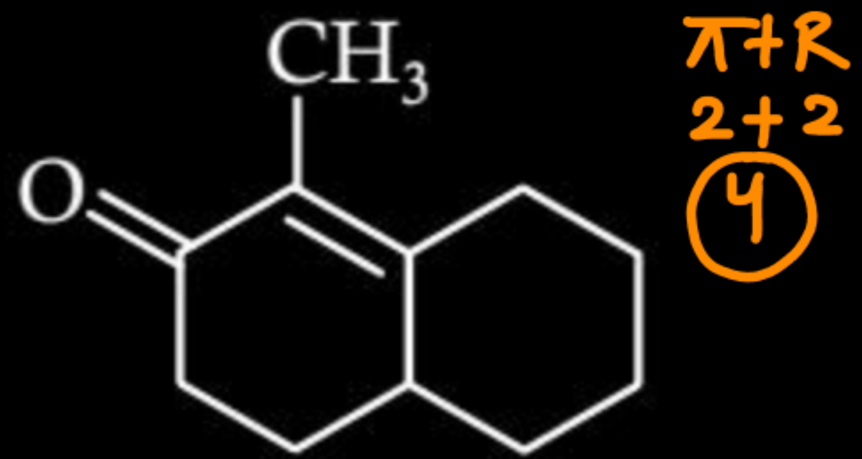
(A) 13

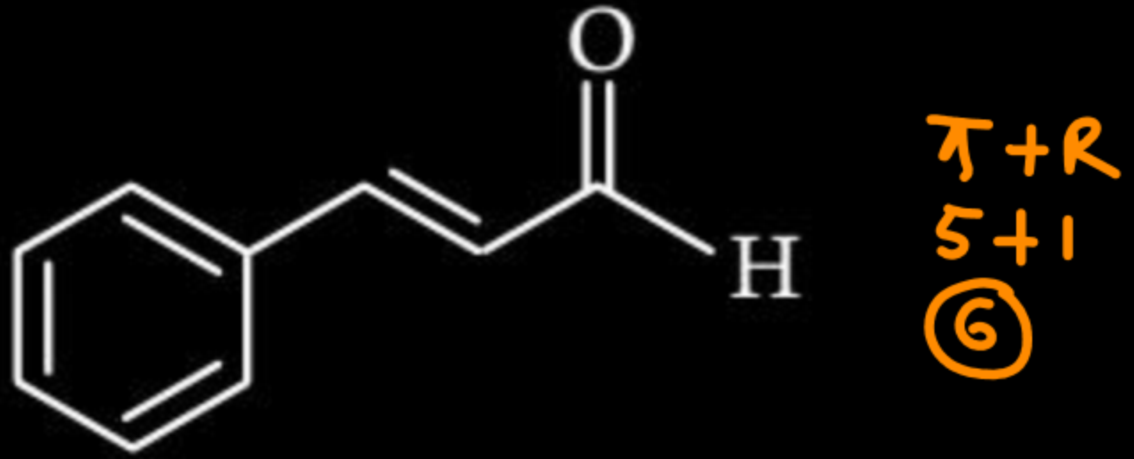
(B) 14 ✓

(C) 15

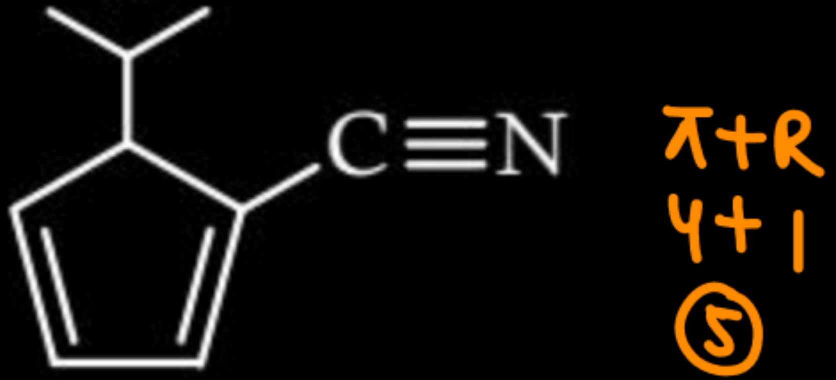
(D) 16

QUESTION:- Rank in order of increasing double bond equivalent (D.B.E.) value or index of hydrogen deficiency (I.H.D.):

(i) 

(ii) 

(iii) 

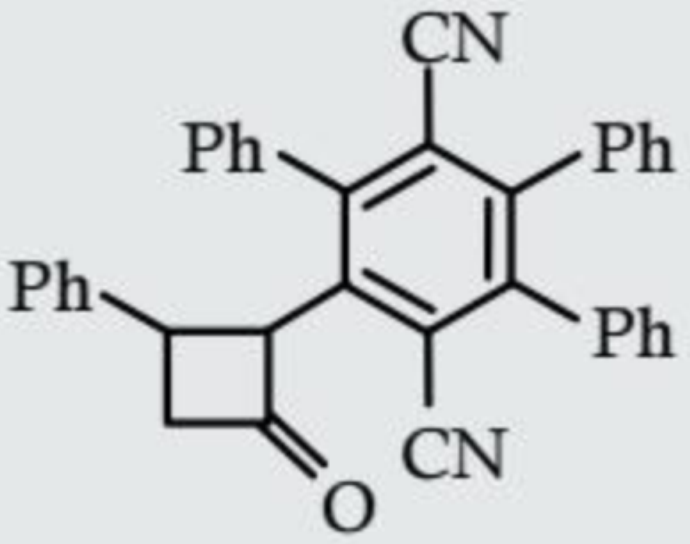
(iv) 

(A) i < iii < ii < iv

(B) i < iii < iv < ii

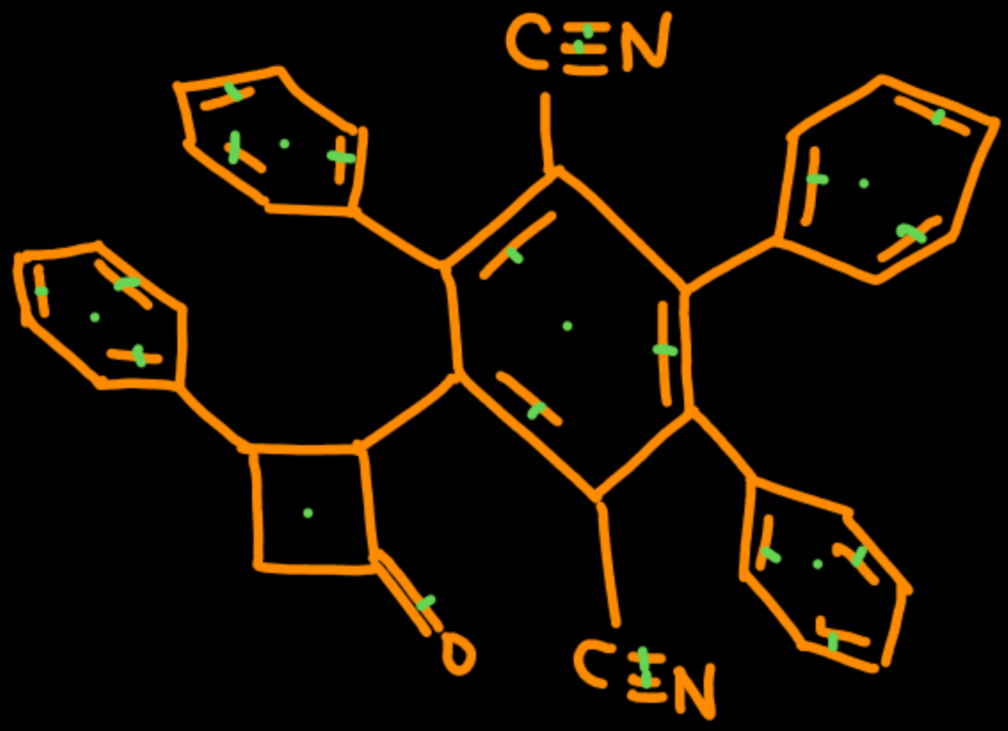
(C) iii < i < iv < ii

(D) iv < iii < ii < i

QUESTION:- Calculate DU of 

is:

π+R
20+6
26

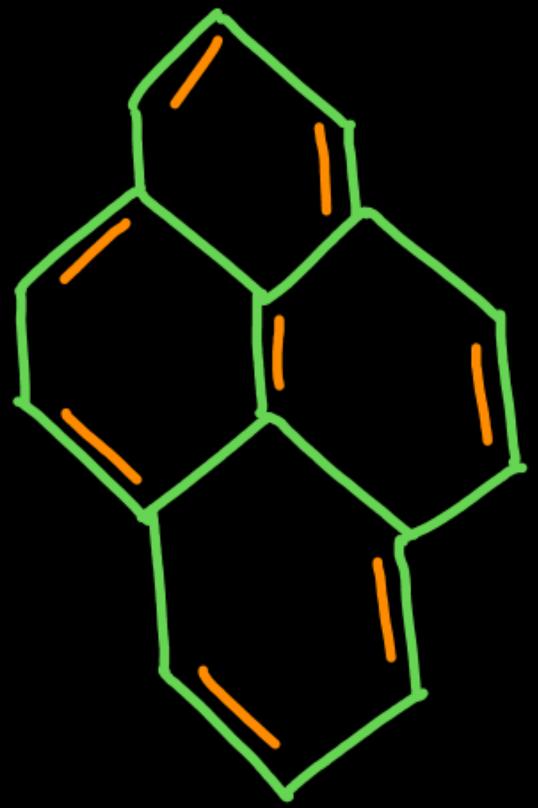


QUESTION:- Calculate DBE of  this compound:

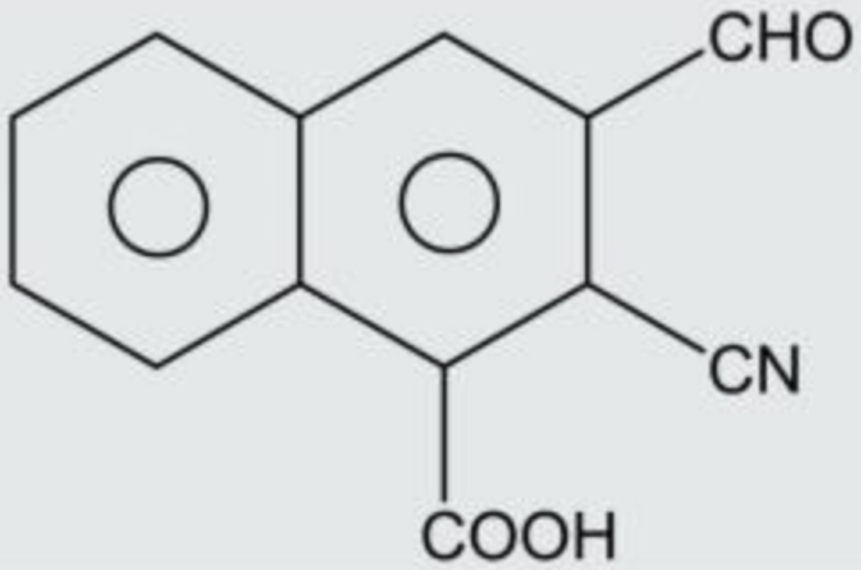
$\pi + R$

$8 + 4$

12



QUESTION:- **Calculate DU:**

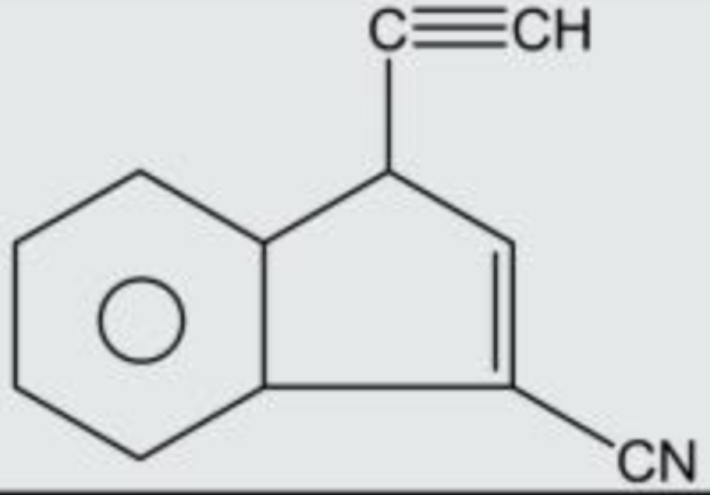


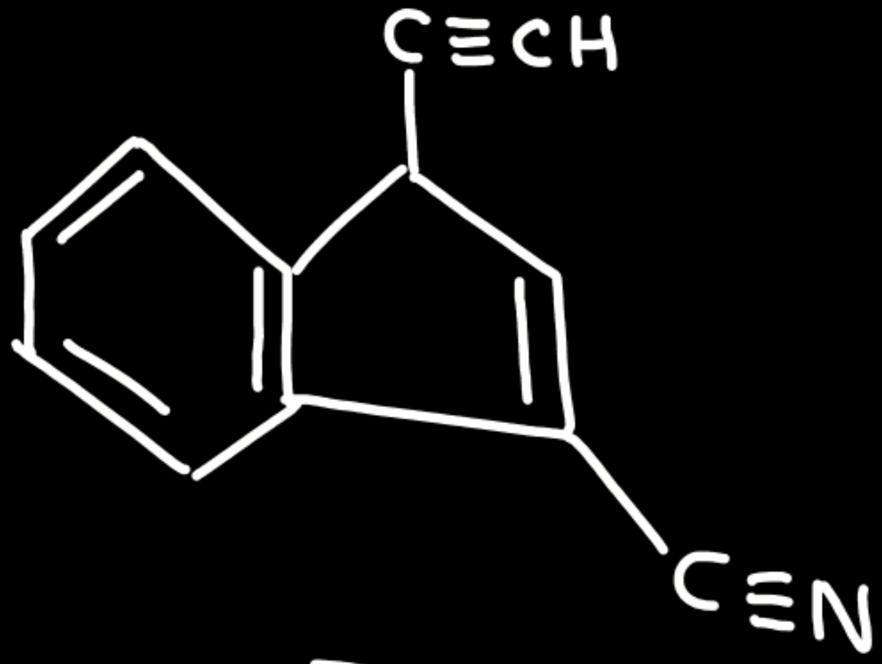
neetPYQ

π + R
9 + 2
11



QUESTION:- **Calculate DU:**



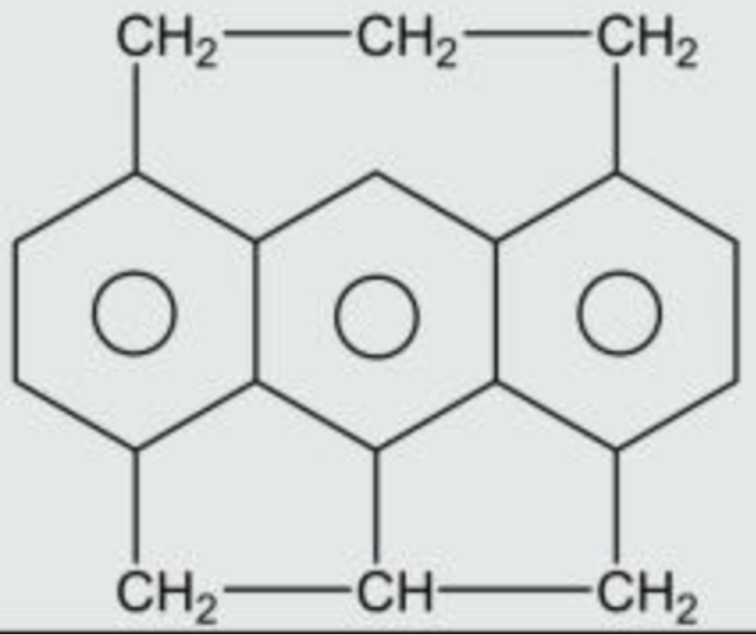


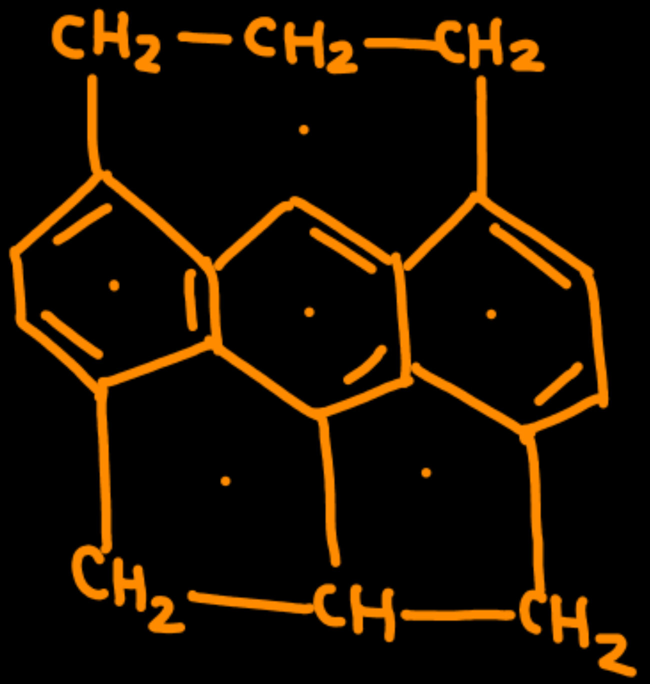
π + R

8 + 2

10

QUESTION:- Calculate DU:





$\pi + R$

$7 + 6$

13

General formula of organic compounds

GF

Alkane → General Formula → C_nH_{2n+2}

Alkene → ,, → C_nH_{2n}

Alkyne → ,, → C_nH_{2n-2}

General Formula → $C_nH_{2n+2-2x} \cdot O_y$

x = DU

y = num of oxy

alkane

DU = x = 0

oxy = y = 0

C_nH_{2n+2}

alkene (C=C)

x = DU = 1

y = oxy = 0

C_nH_{2n}

alkyne C≡C

x = DU = 2

y = oxy = 0

C_nH_{2n-2}

General formula of organic compounds

1. Alcohol

R—OH

$x = DU = 0$

$y = 0xy = 1$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+2} \cdot O$

$C_nH_{2n+1}OH$

2. Ether

R—O—R

$x = DU = 0$

$y = 0xy = 1$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+2} \cdot O$

3. Aldehyde

R—C(=O)—H

$x = DU = 1$

$y = 0xy = 1$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n} \cdot O$

4. Ketone

R—C(=O)—R

$x = DU = 1$

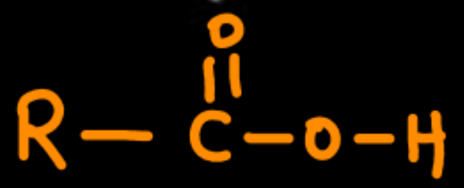
$y = 0xy = 1$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n} \cdot O$

General formula of organic compounds

5. Carboxyllic acid



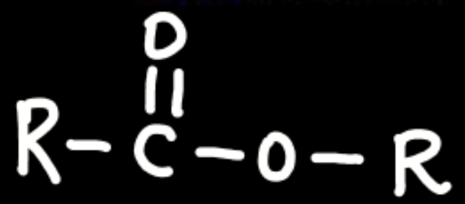
$x = DU = 1$

$y = oxy = 2$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n} \cdot O_2$

6. Ester



$x = DU = 1$

$y = oxy = 2$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n} \cdot O_2$

7. Anhydride



$x = DU = 2$

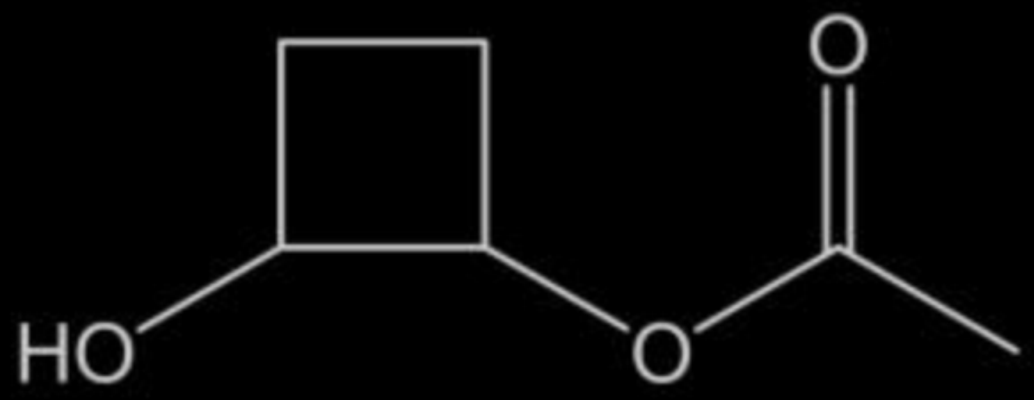
$y = oxy = 3$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+2-4} \cdot O_3$

$C_nH_{2n-2} \cdot O_3$

8.



$DU = \pi + R$

$= 1 + 1$

$= 2$

GF $C_n H_{2n+2-2x} \cdot O_y$

$x = DU = 2$

$y = oxy = 3$

$C_n H_{2n+2-y} \cdot O_3$

$C_n H_{2n-2} \cdot O_3$

10. If DU= any number (More than 2)

enyne $C=C-C\equiv C$ $x = DU = 3$, $y = 0$ $C_nH_{2n+2-2x}\cdot O_y$ $\boxed{C_nH_{2n-4}}$

dienyne $C=C-C=C-C\equiv C$ $x = DU = 4$, $y = 0$ $C_nH_{2n+2-2x}\cdot O_y$ $\boxed{C_nH_{2n-6}}$

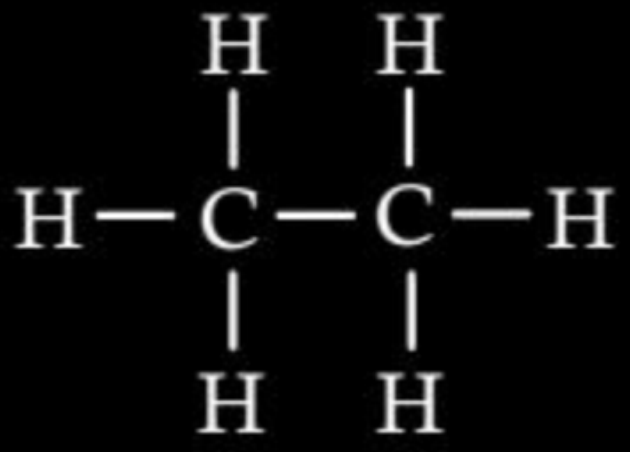
(HW) diene $C=C=C$

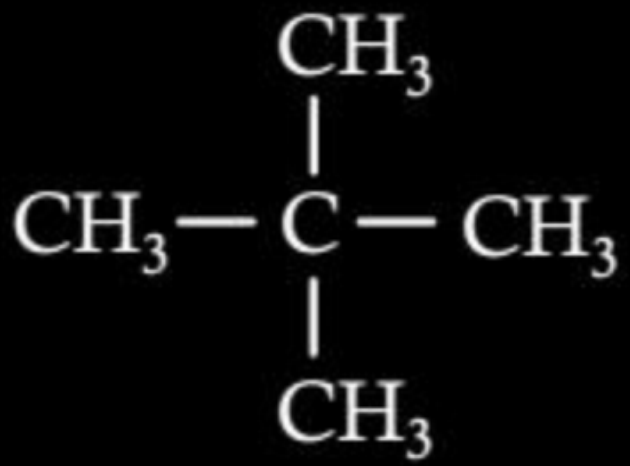
(HW) diyne $C\equiv C-C\equiv C$

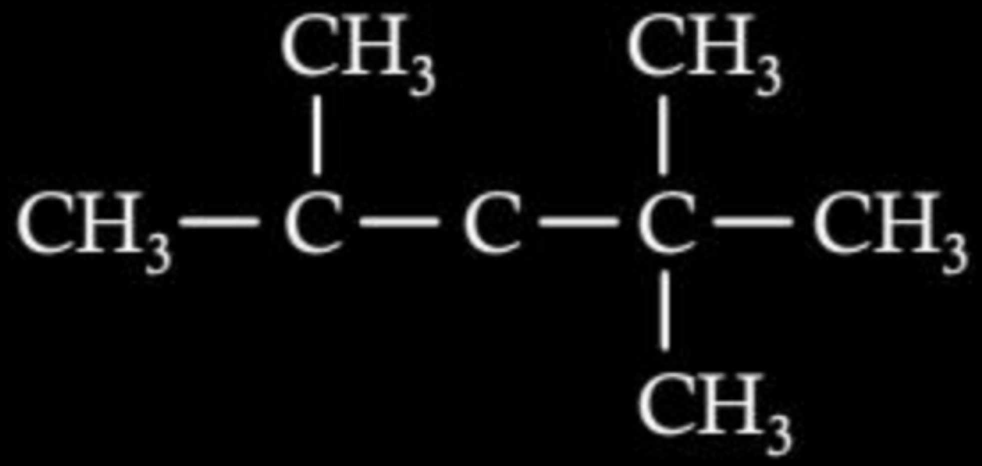
(HW) triyne $C\equiv C-C\equiv C-C\equiv C$

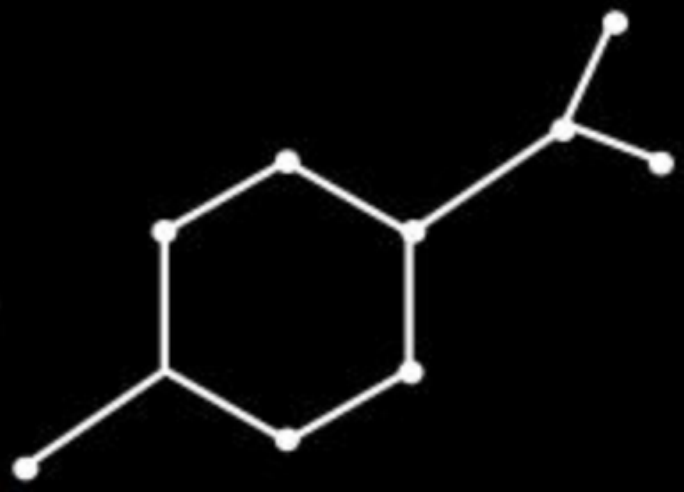
Degree of Carbon

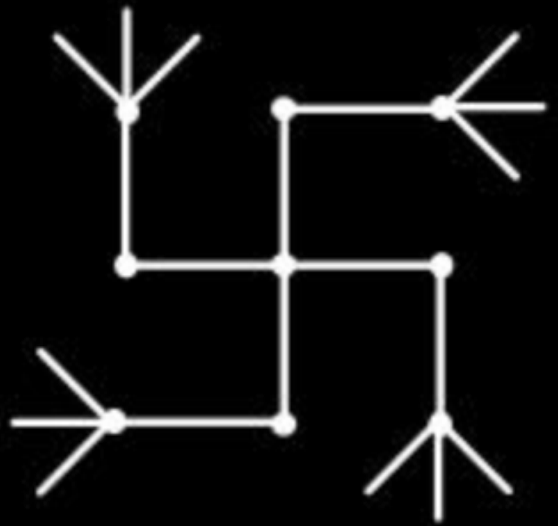
QUESTION:- Find degree of each carbon in the following compound :

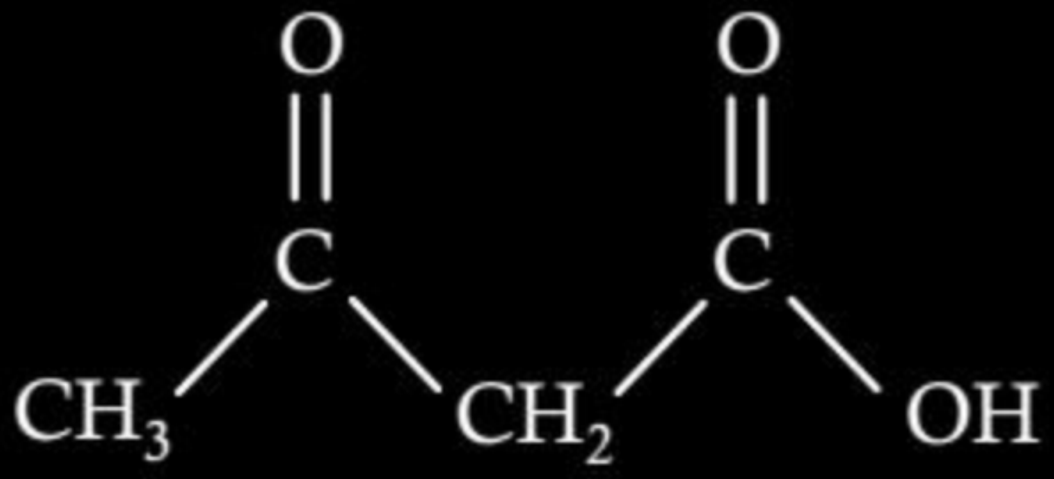
(i) 

(ii) 

(iii) 

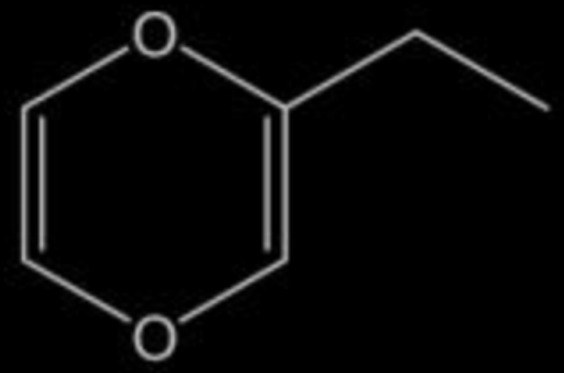
(iv) 

(v) 

(vi) 

QUESTION:- Find degree of each carbon in the following compound :

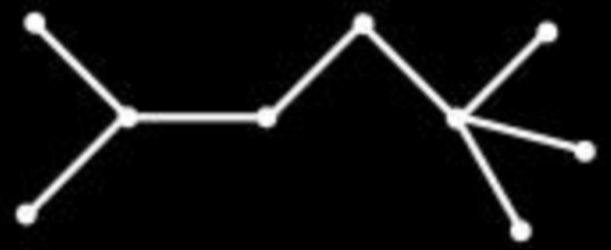
(vii) 

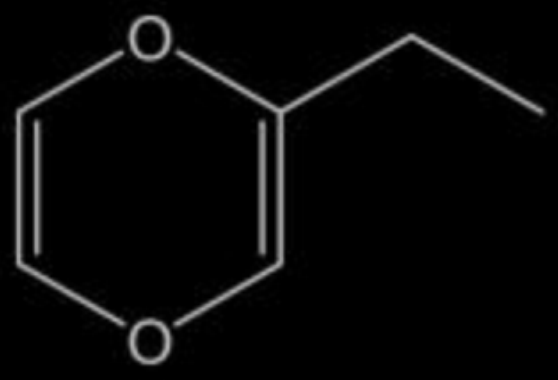
(viii) 

Degree of Hydrogen

QUESTION:- **Calculate degree of hydrogen in the following compound :**





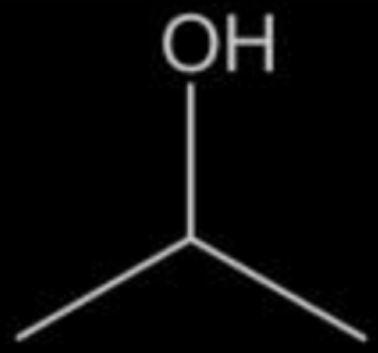


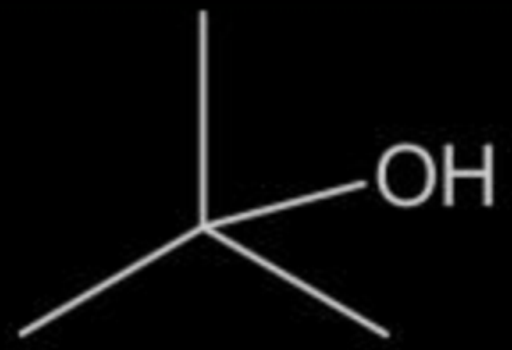
QUESTION:- Write all degree of Carbon & Hydrogen in isooctane-

Degree of Alcohol & Halogen

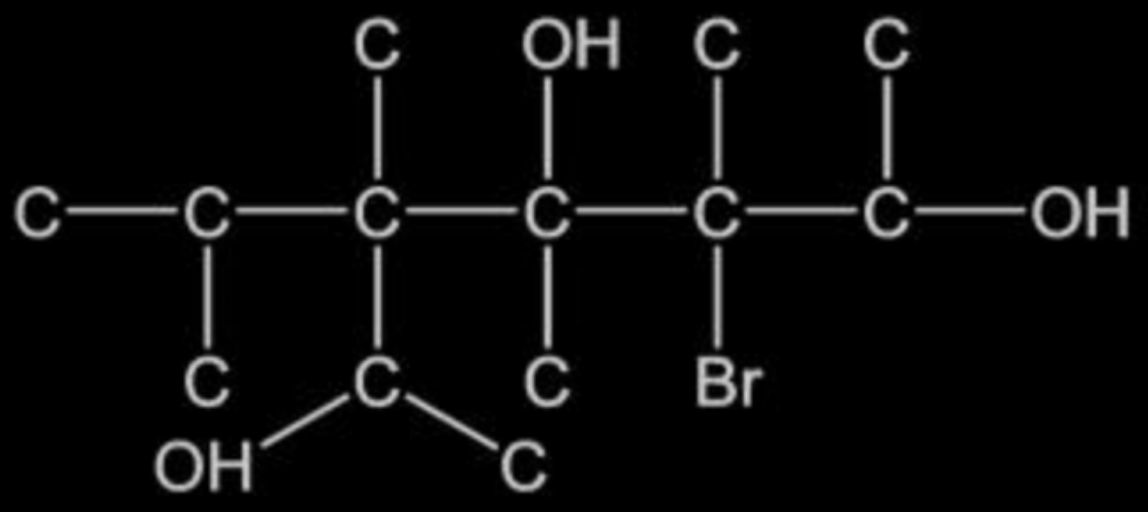
QUESTION:- Write degree of alcohol in following compound-



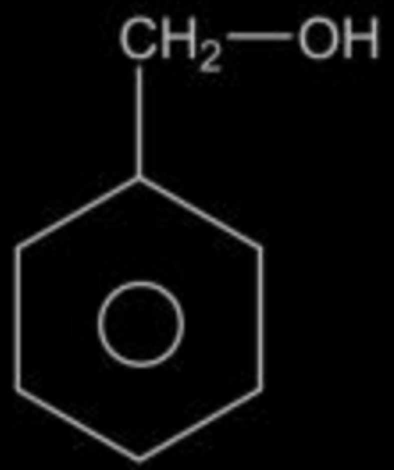


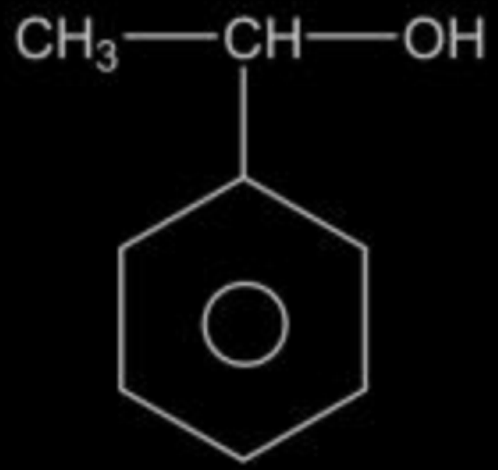


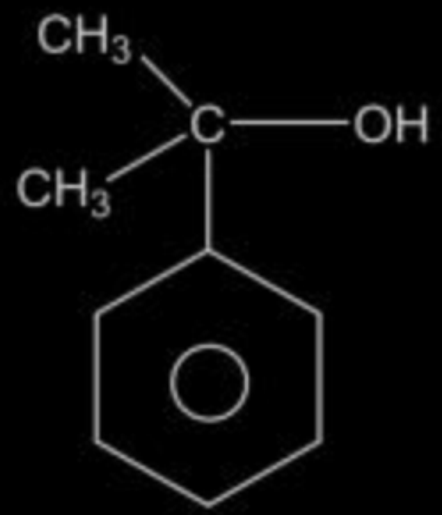
QUESTION:- Write degree of alcohol & Halogen in following compound-



QUESTION:- Write degree of alcohol in following compound-

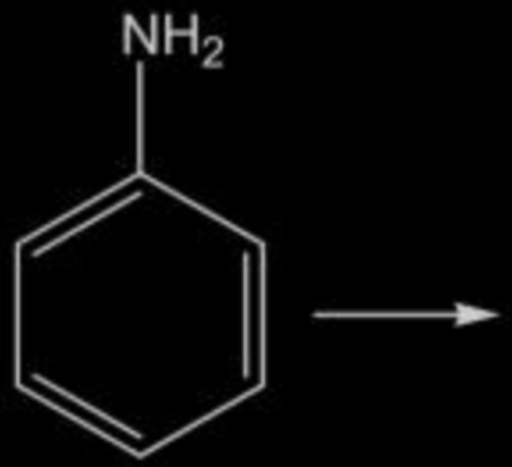




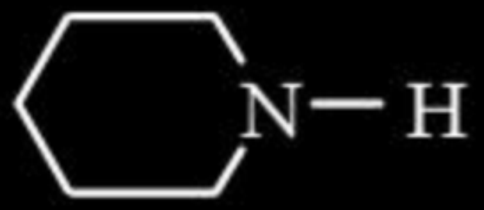


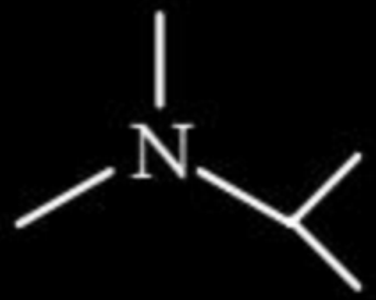


Degree of Amine

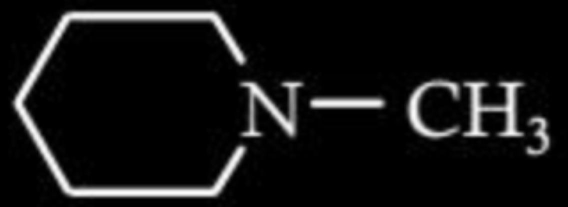
Note ⟹  1° amine

QUESTION:- Indicate the following as 1°, 2° and 3° amines.









Degree of Unsaturation (DU)

QUESTION:- Calculate double bond equivalent (DBE) of following compounds :

(i) $C_{10}H_{10}$

(ii) C_4H_{10}

(iii) C_2H_2

(iv) C_3H_3F

(v) $C_3D_2T_2FCl$

(vi) $C_6HDTF_2ClBr_2$

QUESTION:- Calculate double bond equivalent (DBE) of following compounds :

(vii) C_3O_2

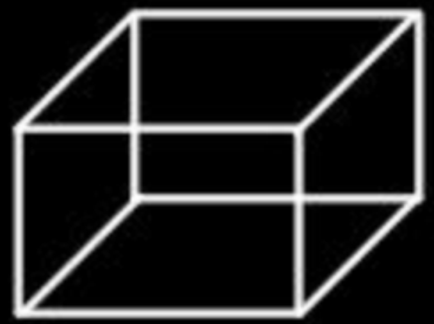
(ix) $C_2H_6N_2$

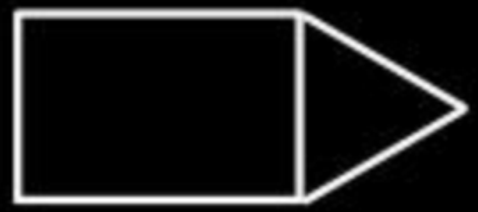
(viii) $C_8H_3Cl_3N_2$

(x) $C_4H_4O_4$

QUESTION:- Calculate double bond equivalent (DBE) of following compounds :

(xi) 

(xii) 

(xiii) 

(iv) 

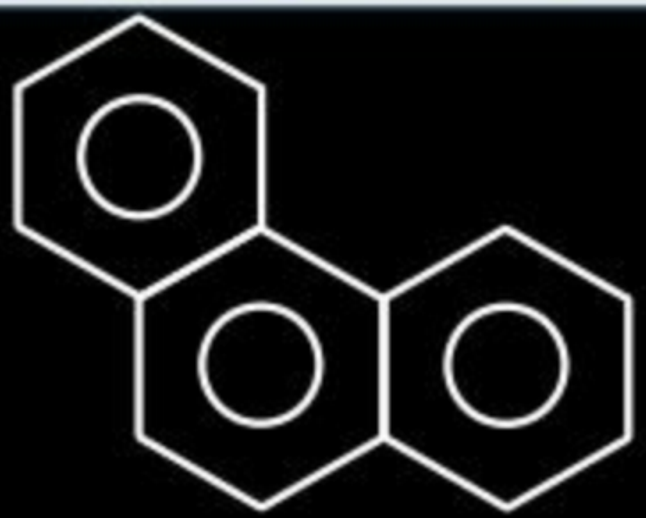
QUESTION:- Calculate double bond equivalent (DBE) of following compounds :

(xii) 

Naphthalene

(xiii) 

Antrancene

(xiv) 

Phenanthacene

QUESTION:- Which of the following compounds has DBE equal to Benzene?

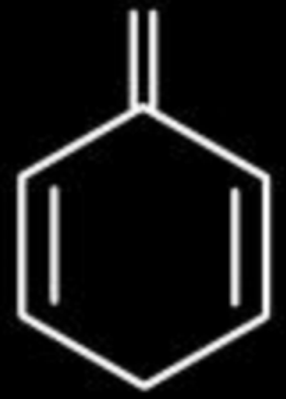
(A)



(B)



(C)

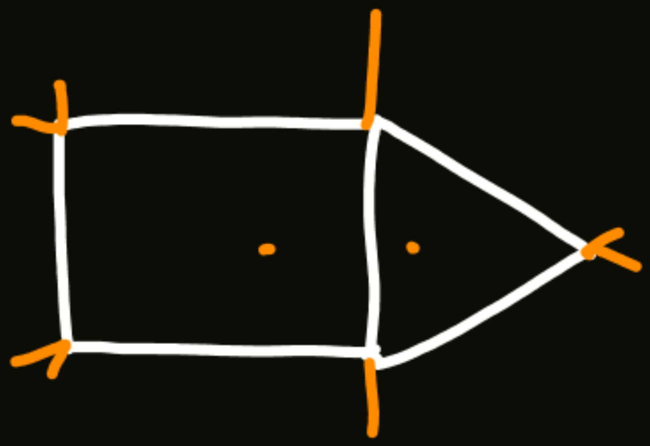


(D) All of these

Degree of Unsaturation

→ Pair of Hydrogen की कमी wrt Alkane. / num of Pi bond & num of Ring.

Formula	Str
$DU = (C+1) - \left(\frac{H+X-N}{2}\right)$	DU = no of π bond + no of Ring



$DU = 2$

$DU = \pi + R$

$= 0 + 2$

$= 2$

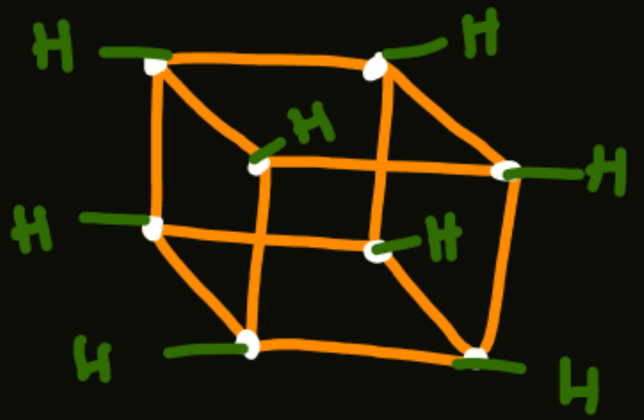
C_5H_8

$$(5+1) - \left(\frac{8+0-0}{2}\right)$$

$$6 - \frac{8}{2}$$

$$6 - 4$$

$$2$$



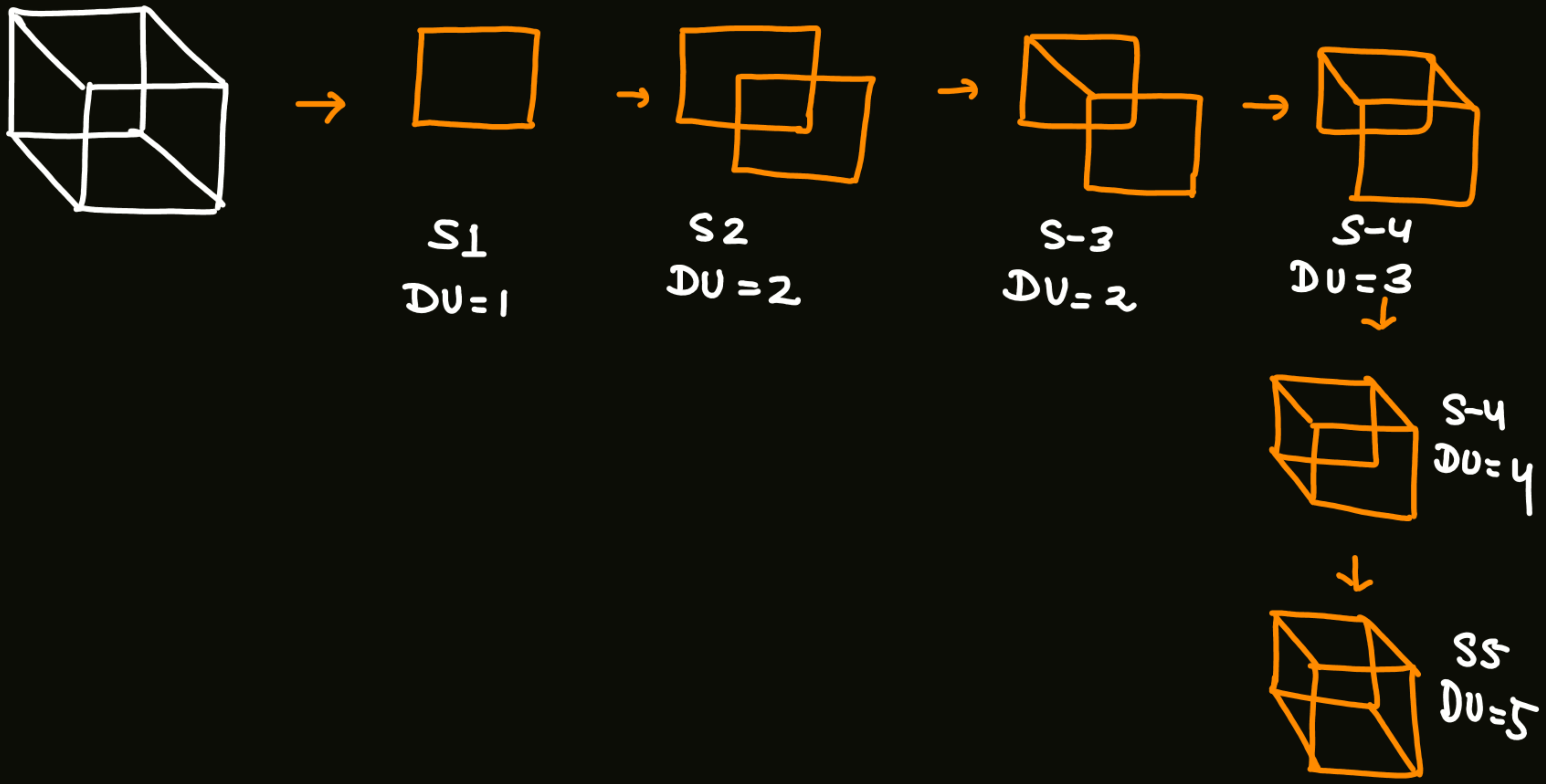
C_8H_8

$$(8+1) - \left(\frac{8+0-0}{2}\right)$$

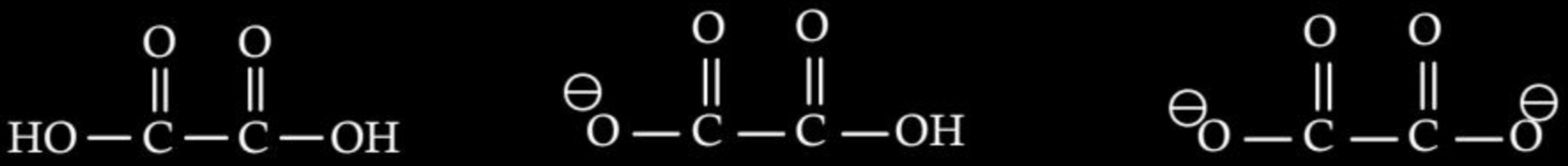
$$9 - \frac{8}{2}$$

$$9 - 4$$

$$5$$


S1
DU=1
S2
DU=2
S-3
DU=2
S-4
DU=3
S-4
DU=4
S5
DU=5

QUESTION:- What is the DBE in the following given structure?



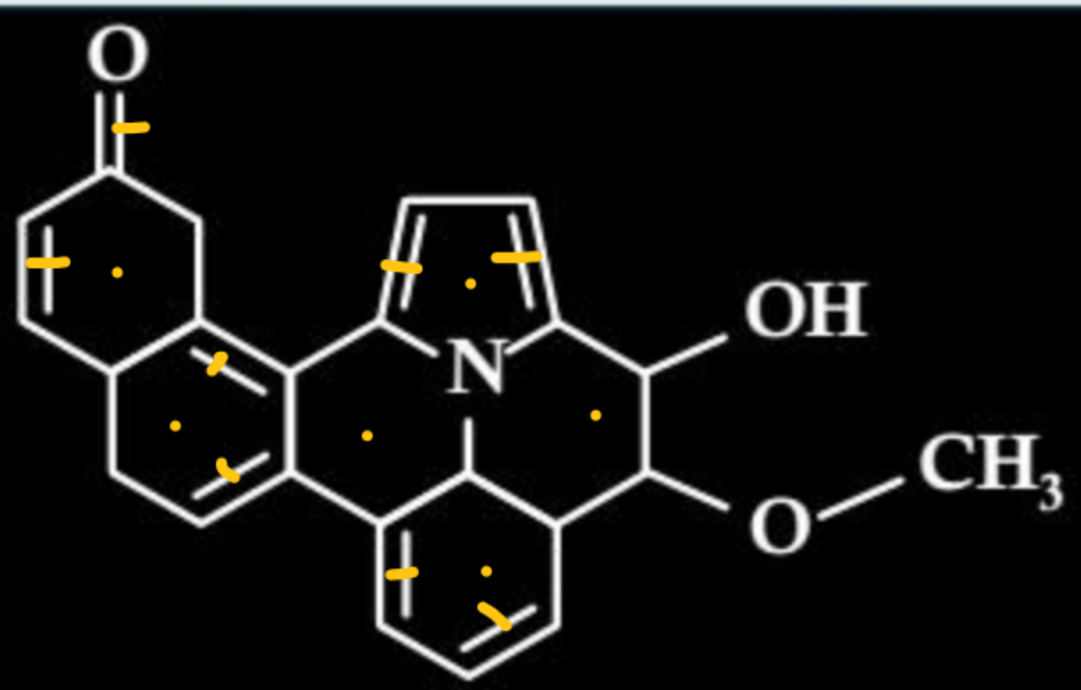
A 2, 3, 4

B 2, 3, 5

C 2, 2.5, 3

D 2, 2.5, 3.5

QUESTION:- Find the DBE (Double Bond Equivalent) of the compound?



DU = π + R
= 8 + 6
= 14

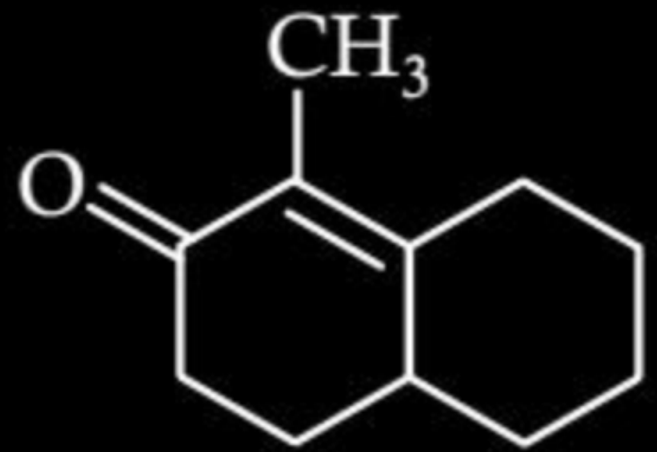
(A) 13

(B) 14 ✓

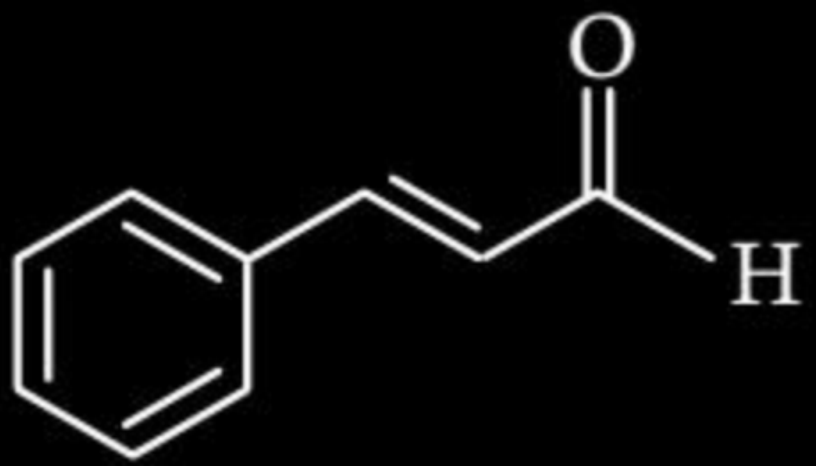
(C) 15

(D) 16

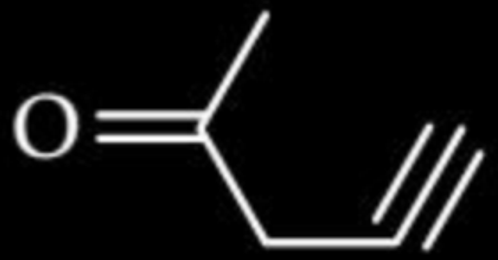
QUESTION:- Rank in order of increasing double bond equivalent (D.B.E.) value or index of hydrogen deficiency (I.H.D.):

(i) 

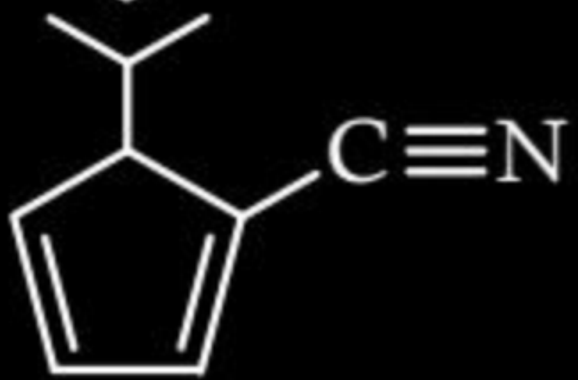
$DU = \pi + R = 2 + 2 = 4$

(ii) 

$DU = \pi + R = 5 + 1 = 6$

(iii) 

$DU = \pi + R = 3 + 0 = 3$

(iv) 

$DU = \pi + R = 4 + 1 = 5$

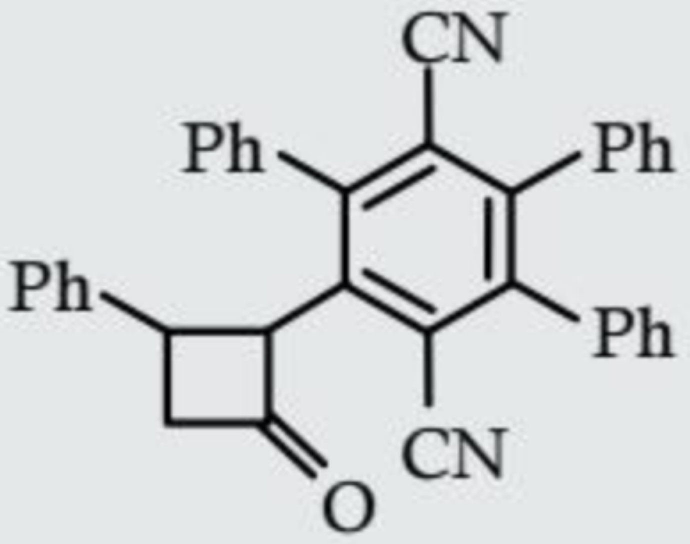
(A) i < iii < ii < iv

(B) i < iii < iv < ii

(C) iii < i < iv < ii ✓

(D) iv < iii < ii < i

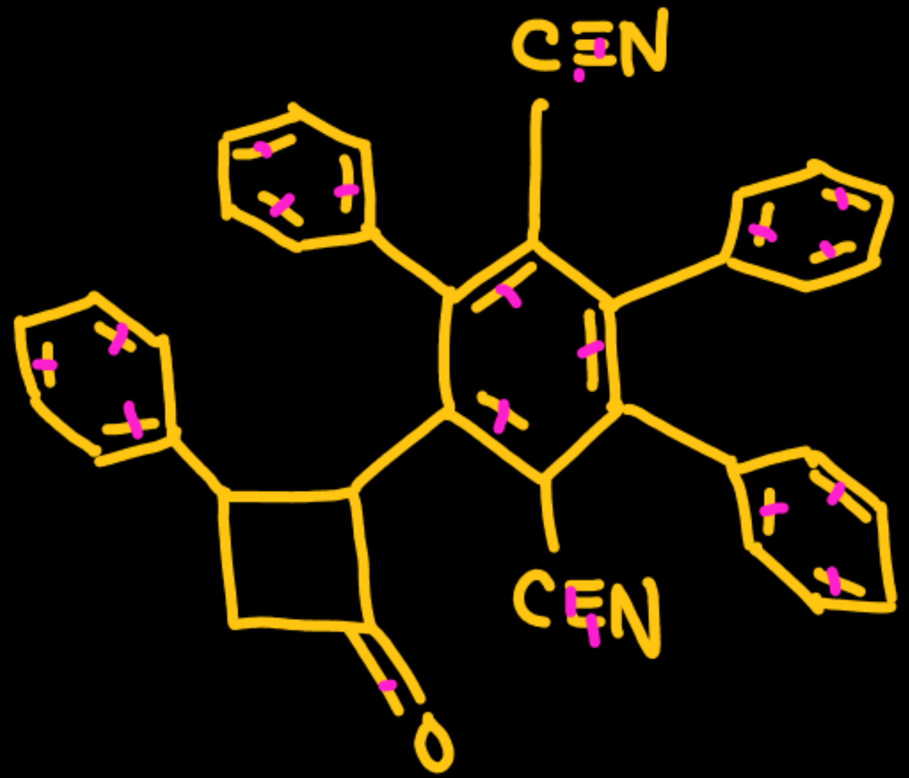
AIIMS

QUESTION:- Calculate DU of  **is:**

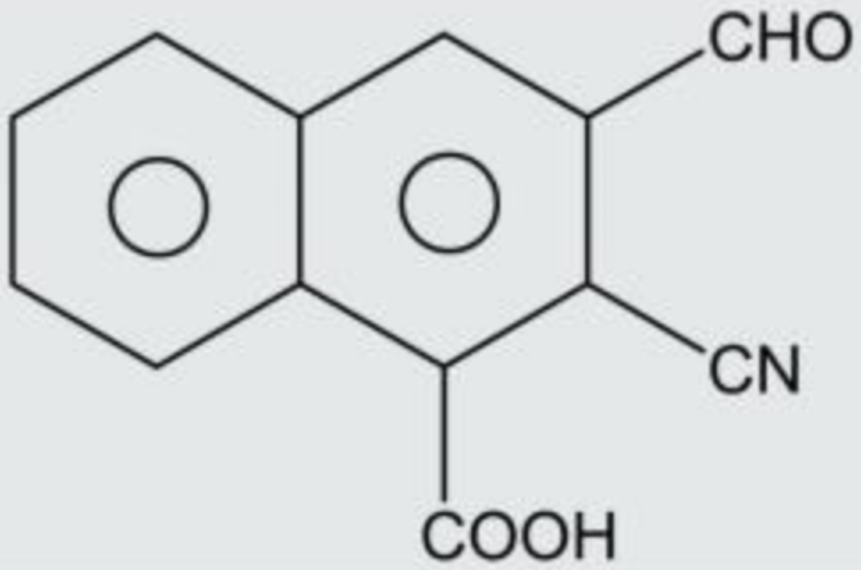
$DU = \pi + R$

$= 20 + 6$

$= 26$



QUESTION:- **Calculate DU:**

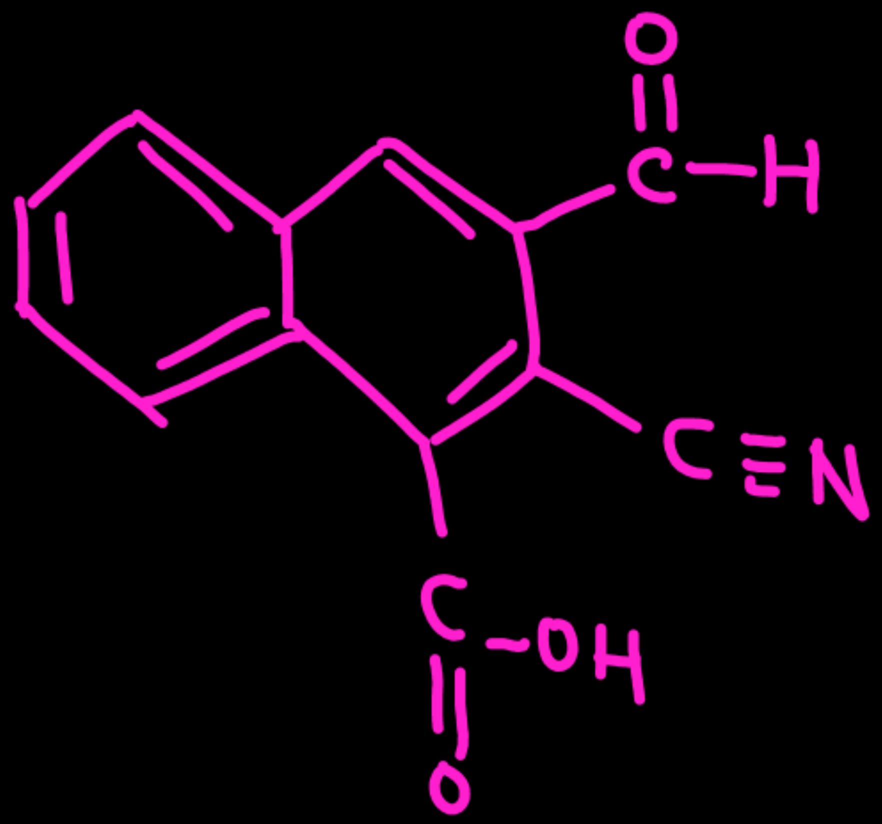


neet

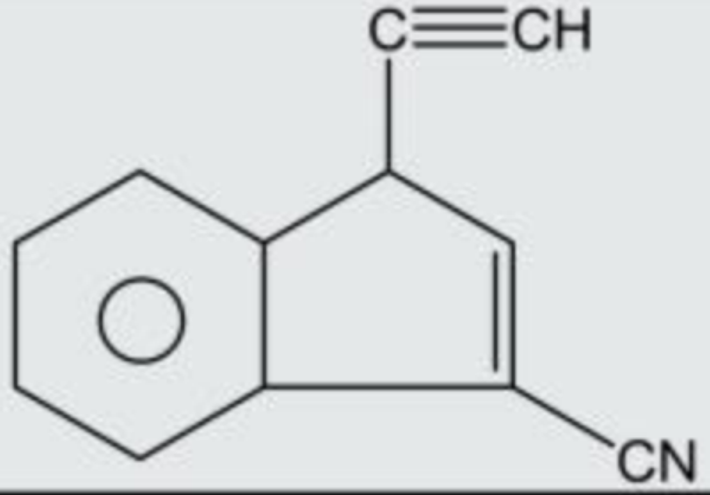
$DU = \pi + R$

$= 9 + 2$

$= 11$

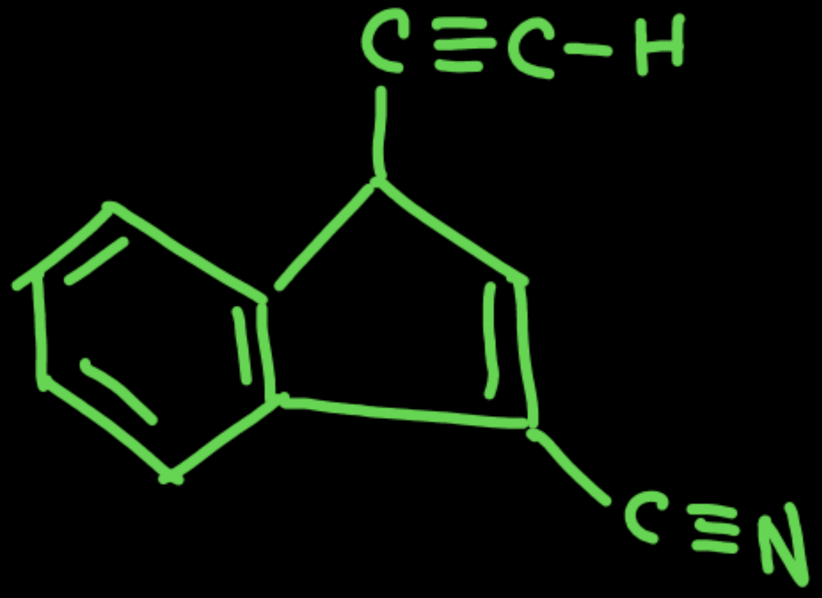


QUESTION:- Calculate DU:

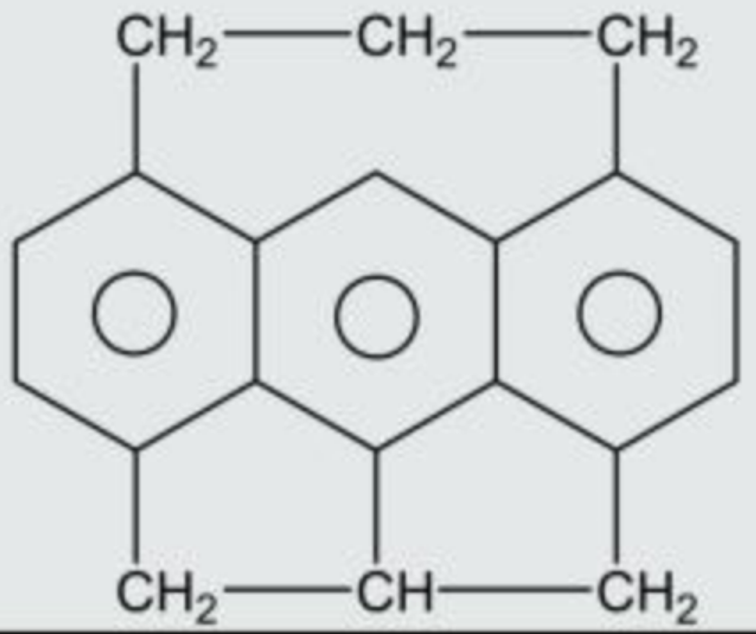


neet

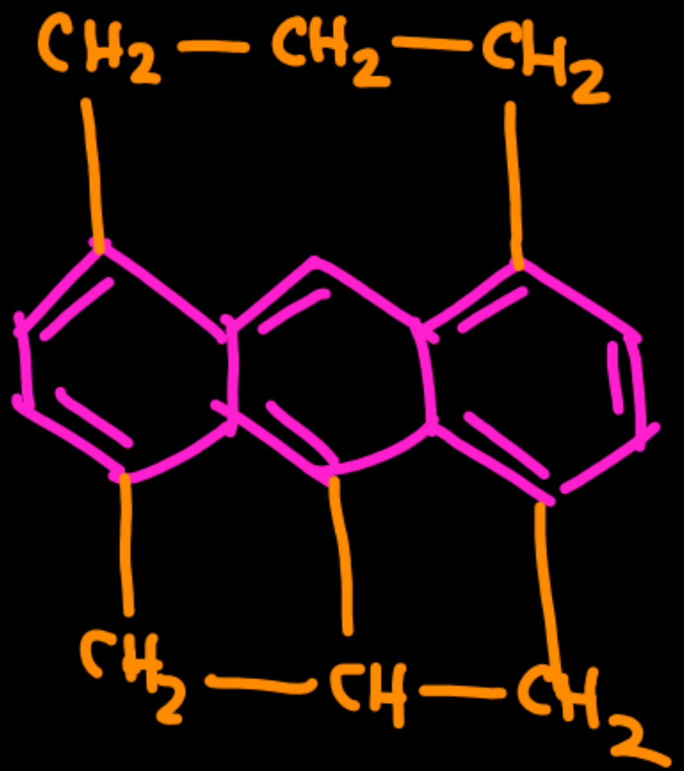
$$DU = \pi + R$$
$$= 8 + 2$$
$$= 10$$



QUESTION:- Calculate DU:



$$DU = \pi + R$$
$$= 7 + 6$$
$$= 13$$



AIPMT

QUESTION:- Which is correct order of DU for Glucose & Sucrose:

A. 2, 2

B. 1, 1

C. 1, 2 ✓

D. 2, 1

Glucose → $C_6H_{12}O_6$

$(6+1)-\left(\frac{12+0-0}{2}\right)$

$7-\frac{12}{2}$

$7-6$

(1)

Sucrose → $C_{12}H_{22}O_{11}$

$(12+1)-\left(\frac{22+0-0}{2}\right)$

$13-\frac{22}{2}$

$13-11$

(2)

General formula of organic compounds

General Formula of any organic Comp → $C_nH_{2n+2-2x} \cdot O_y$

- ✓ n = num of Carbon
- ✓ x = DU
- ✓ y = num of oxygen

① Alkane

DU = 0
oxy = 0

$C_nH_{2n+2-2\times0} \cdot O_0$

→ C_nH_{2n+2}

② Alkene C=C

DU = 1
oxy = 0

$C_nH_{2n+2-2} \cdot O_0$

C_nH_{2n}

③ Alkyne C≡C

DU = 2
oxy = 0

$C_nH_{2n+2-2\times2} \cdot O_0$

C_nH_{2n-2}

General formula of organic compounds

1. Alcohol

R–O–H

DU = 0

oxy = 1

$C_nH_{2n+2-2\times0}\cdot O_1$

$C_nH_{2n+2}\cdot O$

or

$C_nH_{2n+1}\cdot OH$

2. Ether

R–O–R

DU = 0

oxy = 1

$C_nH_{2n+2-2\times0}\cdot O_1$

$C_nH_{2n+2}\cdot O$

3. Aldehyde

R–C(=O)–H

DU = 1

oxy = 1

$C_nH_{2n+2-2\times1}\cdot O_1$

$C_nH_{2n}\cdot O$

4. Ketone

R–C(=O)–R

DU = 1

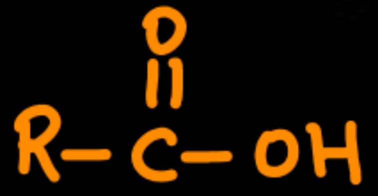
oxy = 1

$C_nH_{2n+2-2\times1}\cdot O_1$

$C_nH_{2n}\cdot O$

General formula of organic compounds

5. Carboxyllic acid



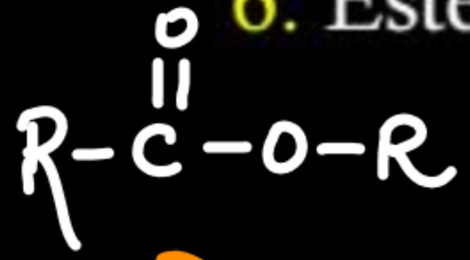
DU = 1

oxy = 2

$C_nH_{2n+2-2\times1}\cdot O_2$

$C_nH_{2n}\cdot O_2$

6. Ester



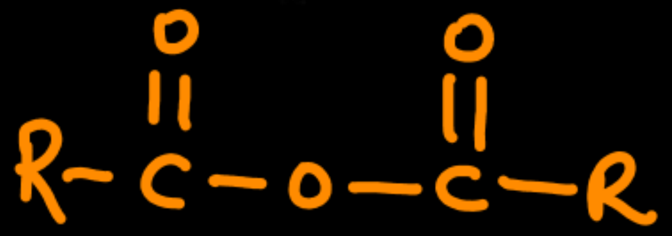
DU = 1

oxy = 2

$C_nH_{2n+2-2\times1}\cdot O_2$

$C_nH_{2n}\cdot O_2$

7. Anhydride



DU = 2

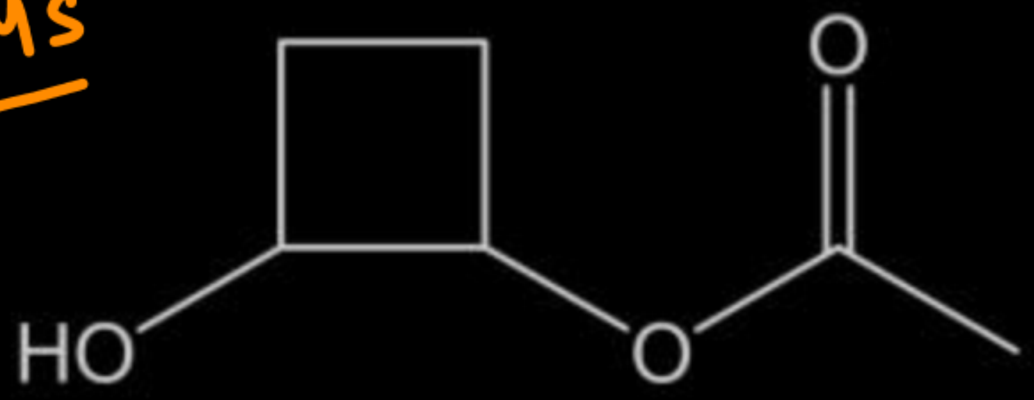
oxy = 3

$C_nH_{2n+2-2\times2}\cdot O_3$

$C_nH_{2n-2}\cdot O_3$

AIIMS

8.



$DU = \pi + R$

$= 1 + 1$

$= 2$

$x = DU = 2$

$y = oxy = 3$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+2-2\times 2} \cdot O_3$

$C_nH_{2n-2} \cdot O_3$

9. Nitrogen containing compounds → add 1 Hydrogen in answer.

Halogen containing compounds → Substract 1 Hydrogen in answer

$R-NH_2$

- $x = DU = 0$
- $y = oxy = 0$
- $C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+2} \cdot N$
$+1$

$C_nH_{2n+3} \cdot N$

R_2NH ($R-N(R)-H$)

$x = DU = 0$

$y = oxy = 0$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+2} \cdot N$
$+1$

$C_nH_{2n+3} \cdot N$

R_3N

$x = DU = 0$

$y = oxy = 0$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+2} \cdot N$
$+1$

$C_nH_{2n+3} \cdot N$

$R-X$

$x = DU = 0$

$y = oxy = 0$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+2} \cdot X$
-1

$C_nH_{2n+1} \cdot X$

10. If DU= any number (More than 2)

eneyne	$\{ = \quad \equiv \}$	$x = DU = 3$ $y = 0 \times y = 0$	$C_nH_{2n+2-2x} \cdot O_y$ $C_nH_{2n+2-2\times3}$ C_nH_{2n-4}
diene	$\{ = \quad = \}$	$x = DU = 2$ $y = 0 \times y = 0$	$C_nH_{2n+2-2\times2} \cdot O_y$ C_nH_{2n-2}
diyne	$\{ \equiv \quad \equiv \}$	$x = DU = 4$ $y = 0$	$C_nH_{2n+2-2\times4} \cdot O_y$ C_nH_{2n-6}
triyne	$\{ \equiv \quad \equiv \quad \equiv \}$	$x = DU = 6$ $y = 0$	$C_nH_{2n+2-2x} \cdot O_y$ $C_nH_{2n+2-12}$ C_nH_{2n-10}

Functional Group

Functional Group ↴

Atom/Group of atom which decides the chemical properties of an organic compound.
(chemical reaction)

Ex →

$H_3C-CH_2-\boxed{OH}$

$H_3C-CH_2-\boxed{COOH}$

$H_3C-CH_2-\boxed{\ddot{N}H_2}$

$H_3C-CH_2-\boxed{X}$

Functional Group

1. Alkene $>C=C<$
2. Alkyne $-C\equiv C-$
3. Arene 
4. Halide $R-X$
5. Nitro $R-NO_2$
6. Nitrite $R-ONO$
7. Nitroso $R-NO$

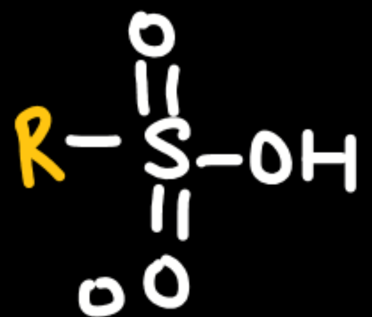
8. Alcohol $R-OH$

9. Thios/Thioalcohol $R-SH$

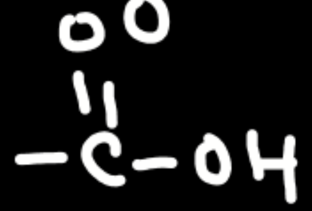
10. Ether $R-O-R$

11. Thioether $R-S-R$

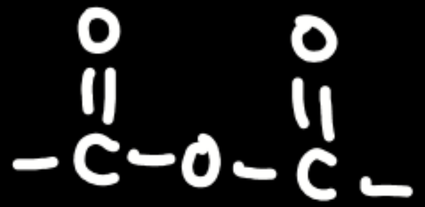
12. Sulphonic acid $R-SO_3H$



13. Carboxylic acid $-COOH$ $-CO_2H$



14. Acid anhydride $-C_2O_3$



15. Aldehyde $-CHO$



16. **Ketone** $R-CO-R$ $\quad R-C(=O)-R$

17. **Nitrile/Cyanide** $-CN$ $\quad -C\equiv N$

18. **Isonitrile/Isocyanide** $-NC$ $\quad -N\equiv C$

19. **Ester** $-COOR$ $\quad -CO_2R$ $\quad -C(=O)-O-R$

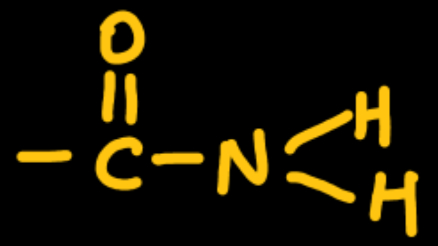
20. **Acid halide** $-COX$ $\quad -C(=O)-X$

21. **1° amine** $R-NH_2$

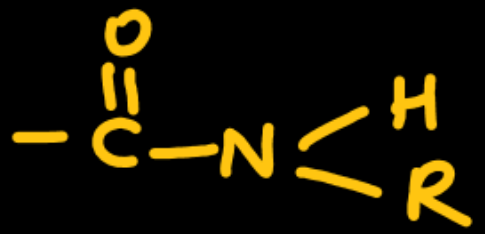
22. **2° amine** R_2NH

23. **3° amine** R_3N

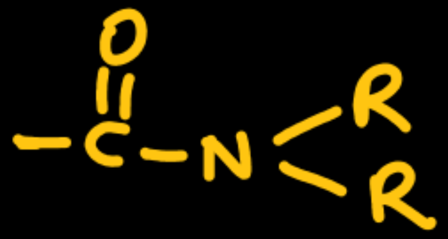
24. 1° amide — $-CONH_2$



25. 2° amide — $-CONH-R$



26. 3° amide — $-CONR_2$



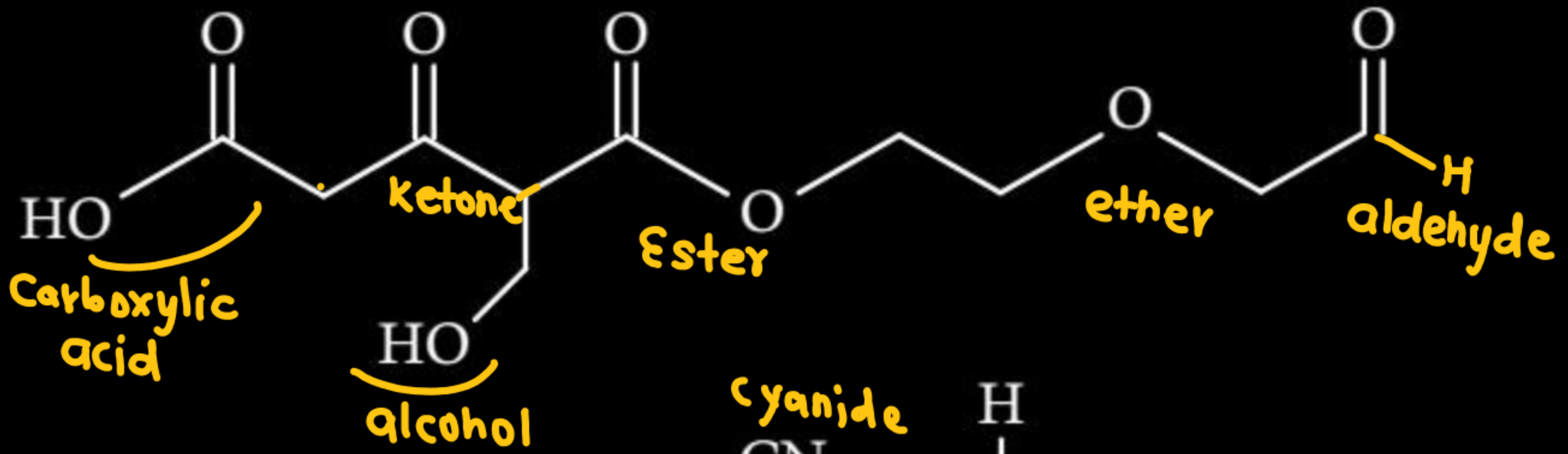
27. Epoxy



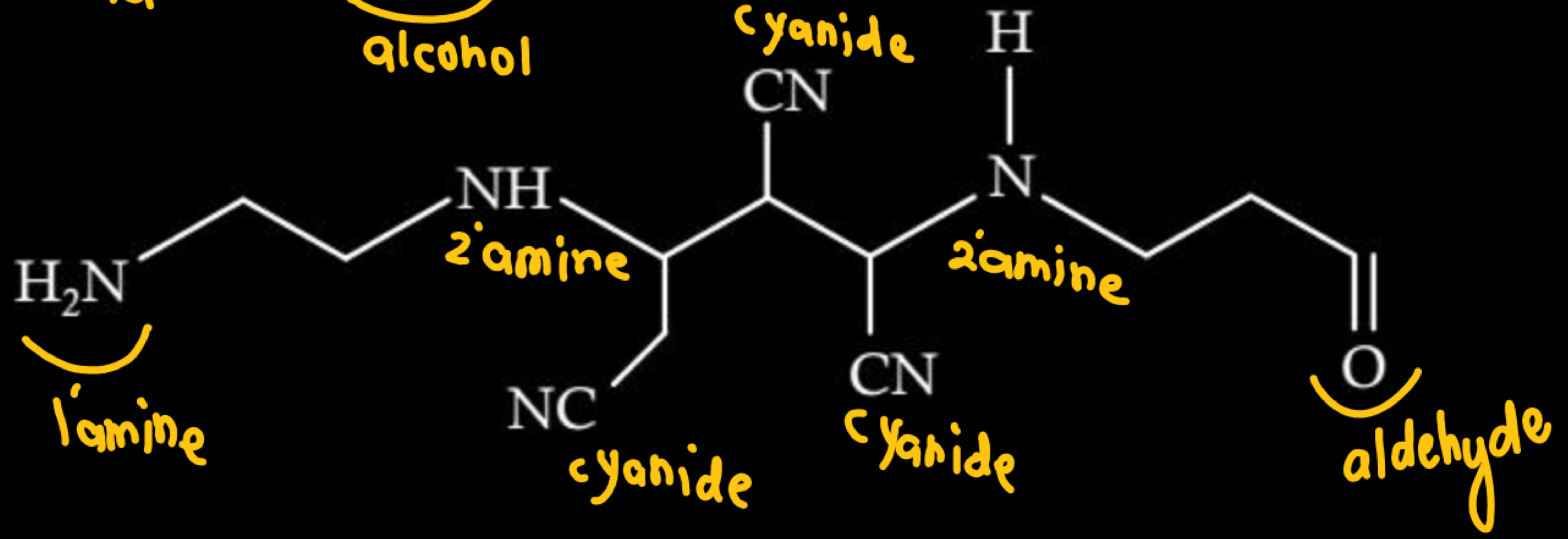
28. Azo — $-N=N$

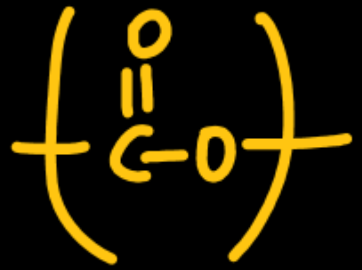
QUESTION:- Count the number of distinct functional group:

6 (i)

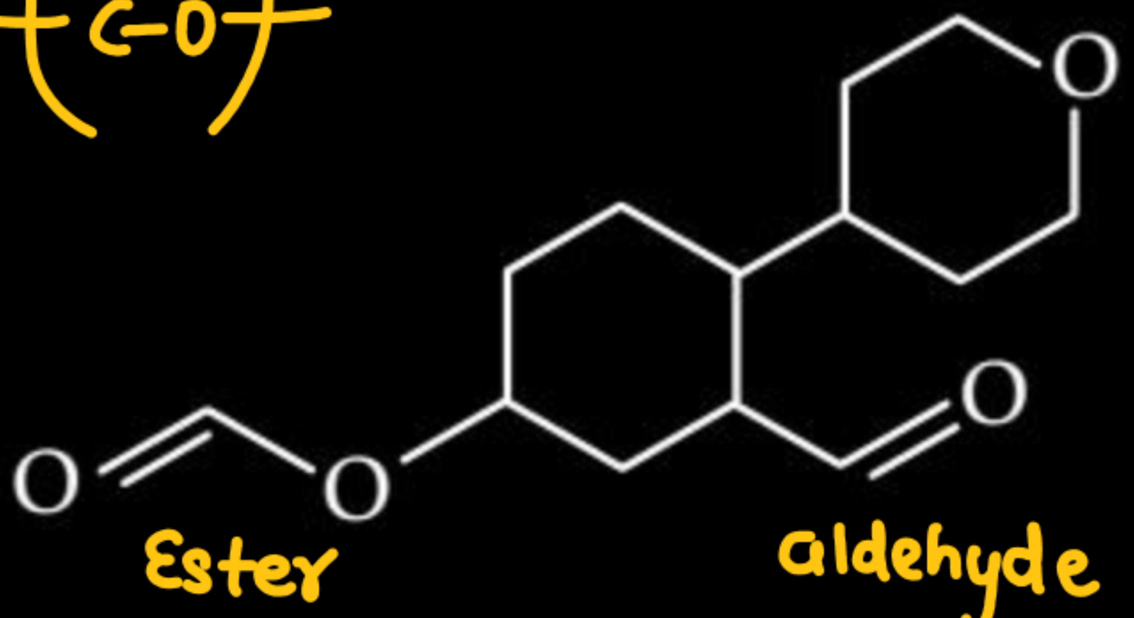


4 (ii)

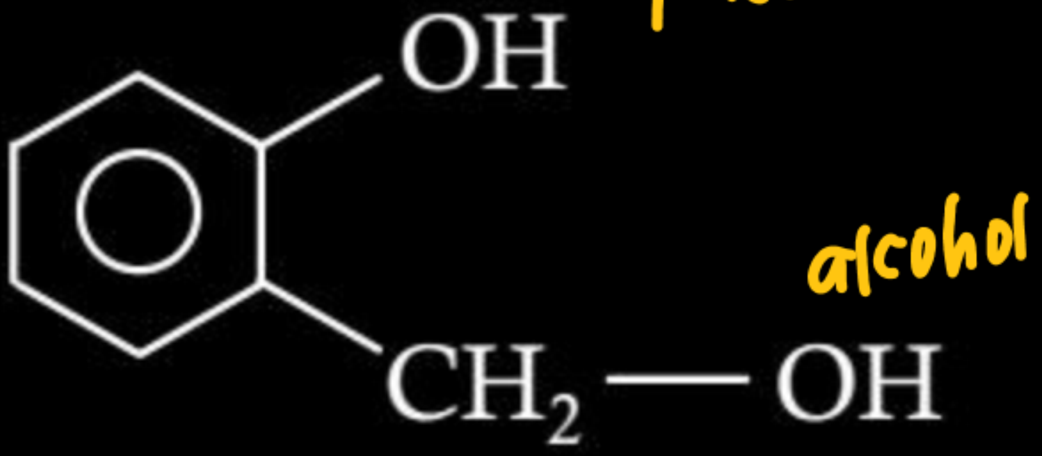




3
(iii)



2
(iv)



1° halogen
2° halogen
3° halogen } Same FG

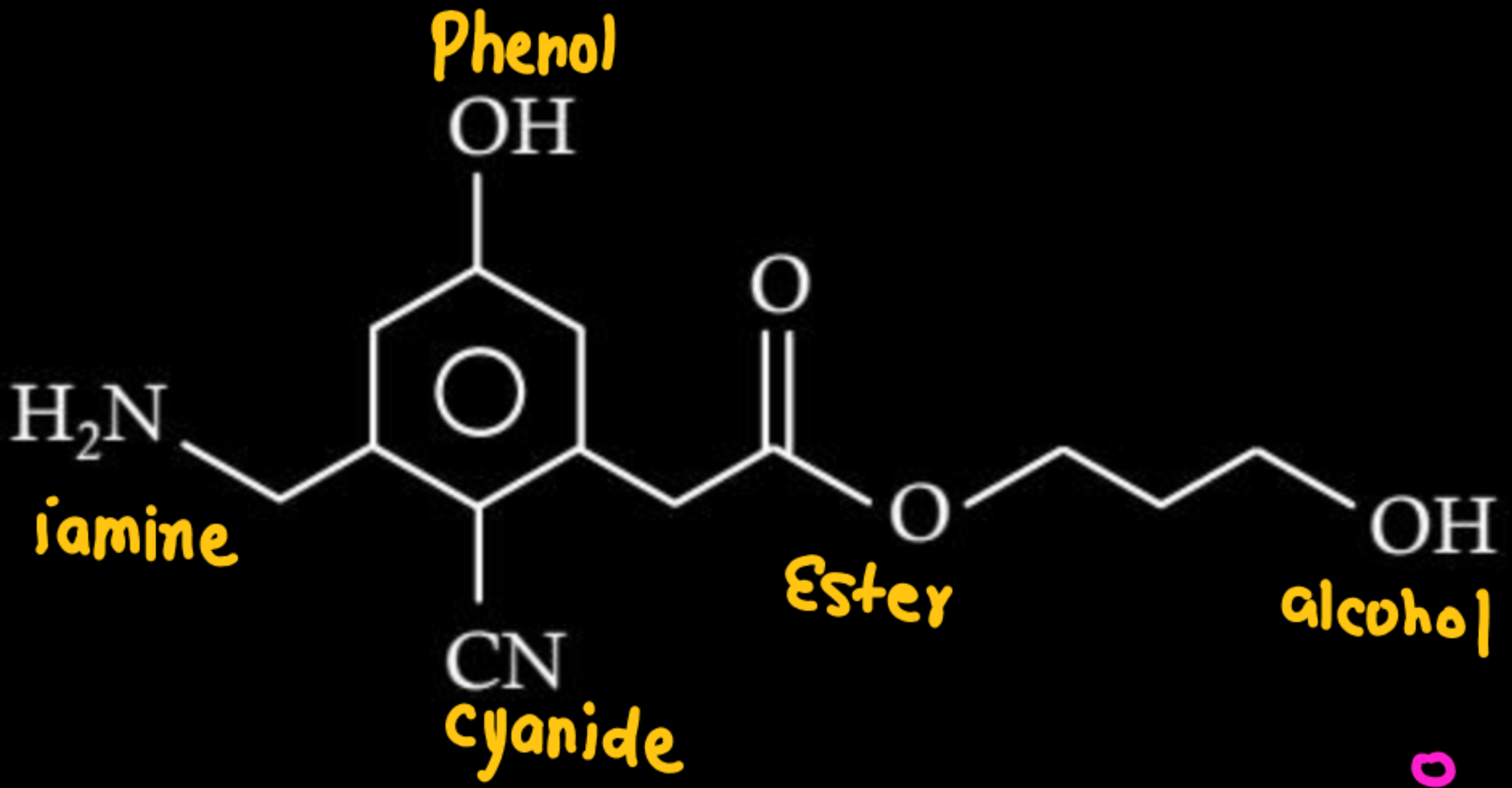
1° alcohol
2° alcohol
3° alcohol } Same FG

Note → alcohol & phenol are 2 diff FG

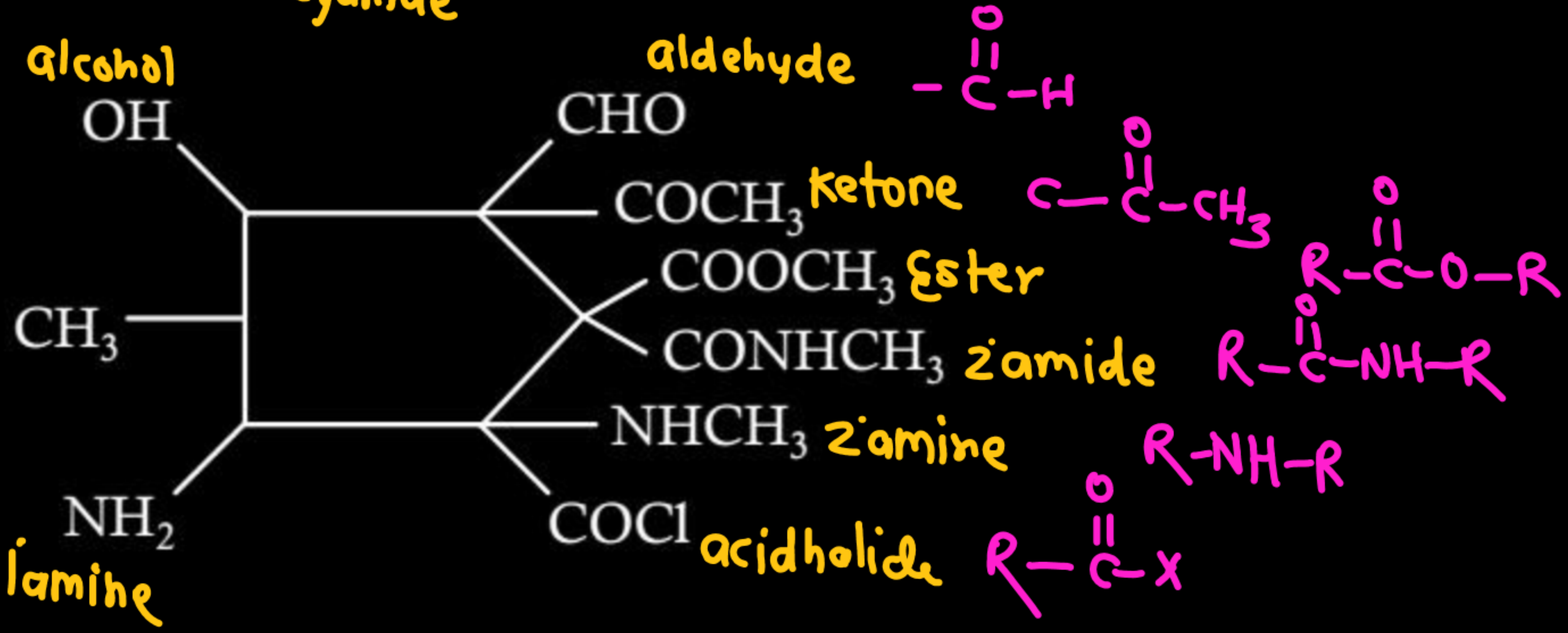
→ 1° amine, 2° amine, 3° amine are 3 diff FG

→ 1° amide, 2° amide, 3° amide are 3 diff FG.

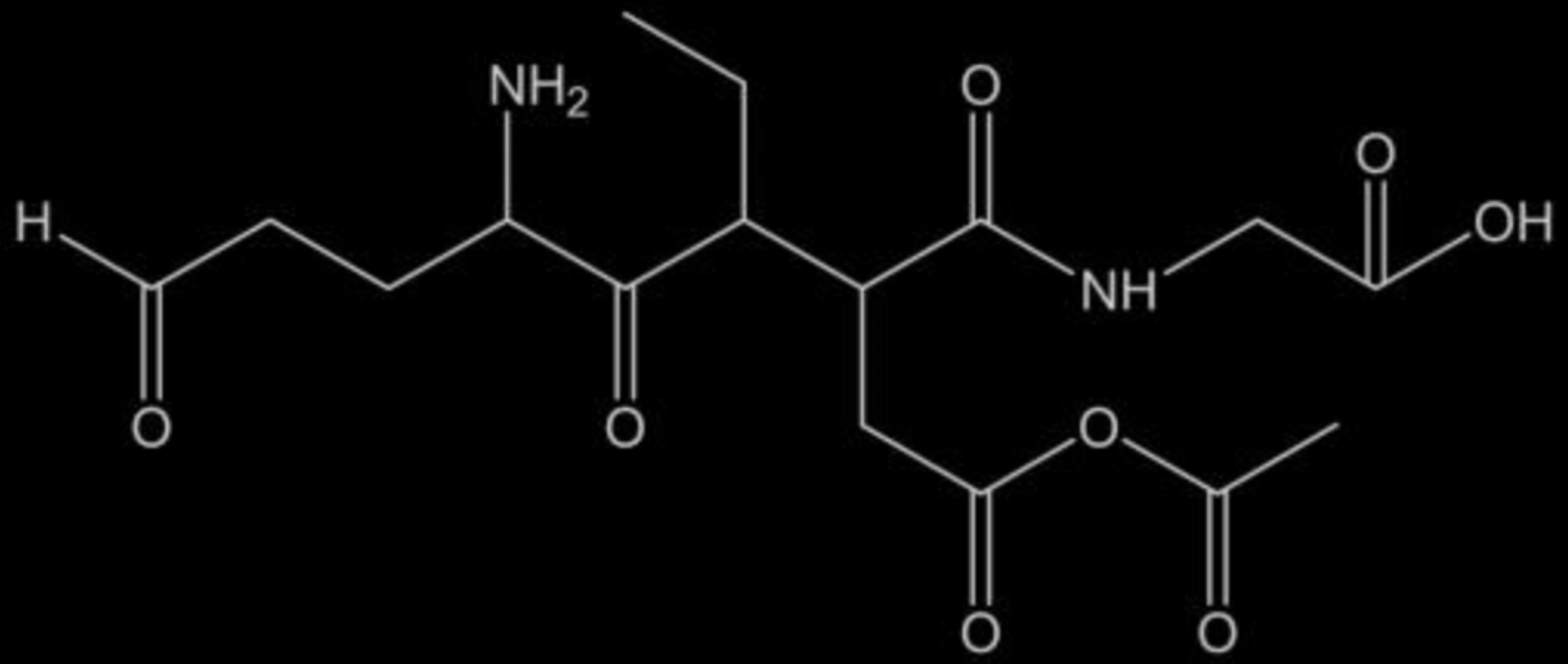
5 (v)


Phenol
OH
O
H_2N
iamine
O
OH
Ester
alcohol
CN
cyanide

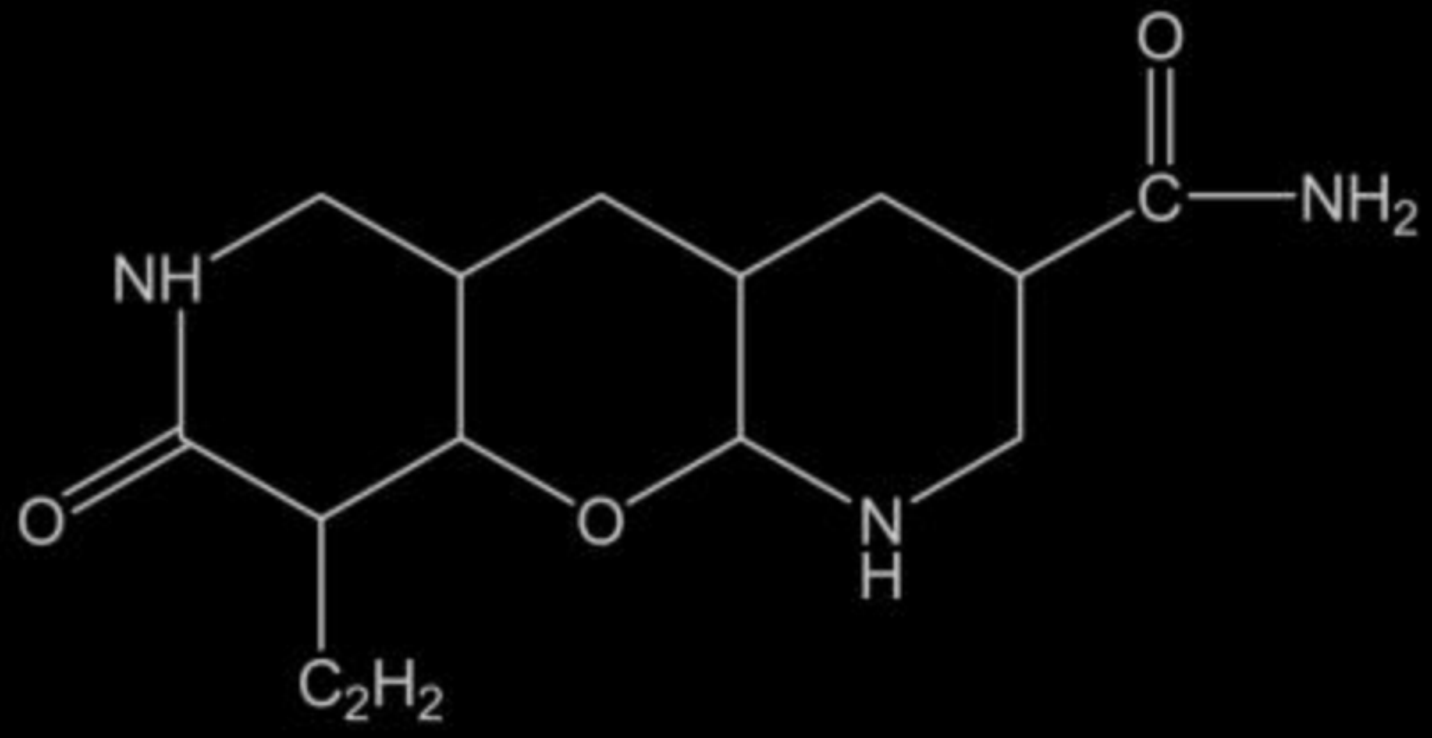
8 (vi)


alcohol
OH
aldehyde
CHO
$COCH_3$ ketone
$COOCH_3$ Ester
$CONHCH_3$ 2°amide
CH_3
$NHCH_3$ 2°amine
NH_2
l°amine
COCl acidhalide
R—NH—R

(vii)



(viii)



Thank you
Future Doctors!!

Degree of Unsaturation

Functional Group

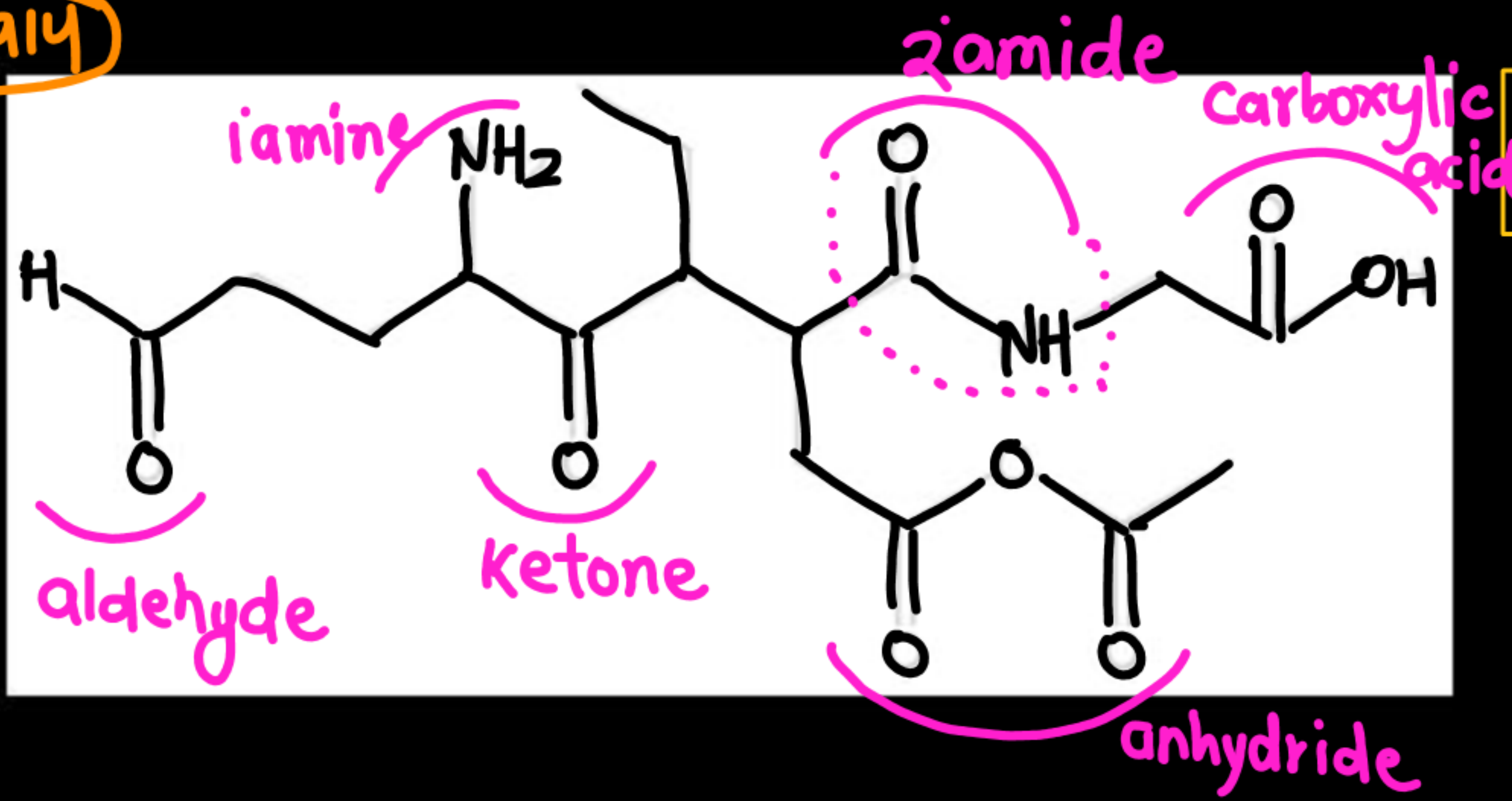
General Formula of Organic Comp

7877921914

Number of Functional Group

6

(vii)



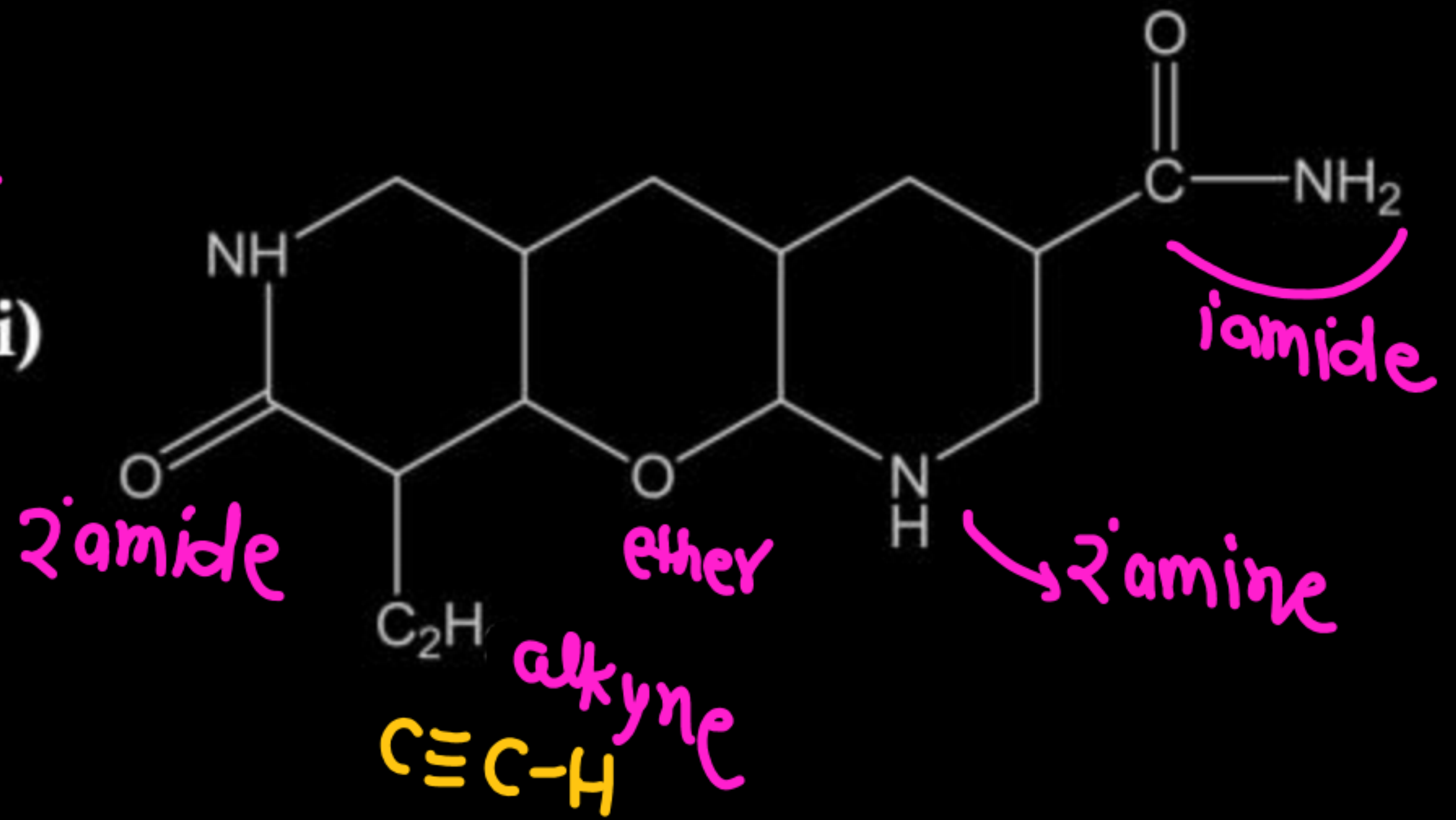
$H/R-\overset{O}{\overset{\|}{C}}-NH_2$ 1° amide

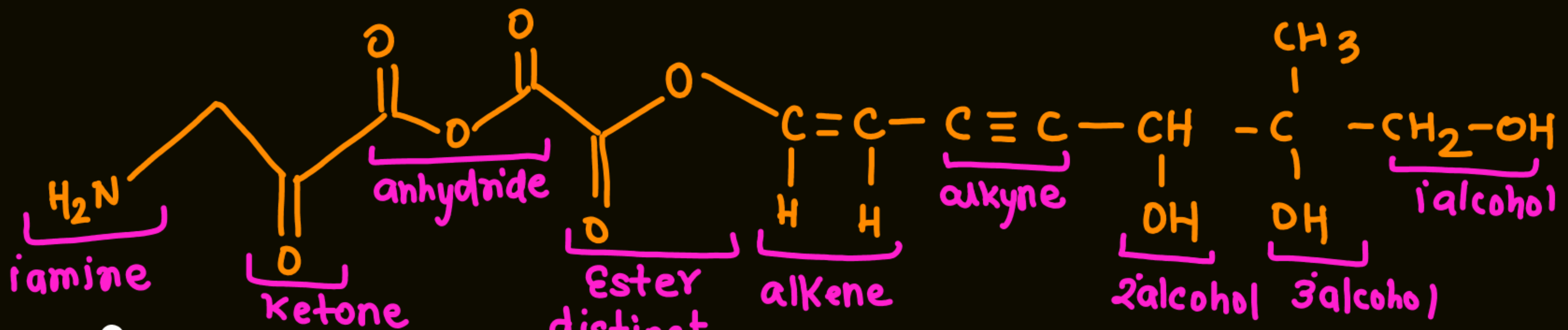
$H/R-\overset{O}{\overset{\|}{C}}-NH-R$ 2° amide

$H/R-\overset{O}{\overset{\|}{C}}-NR_2$ 3° amide

5

(viii)





Count the number of distinct functional groups in the compound—

(A) 9

(B) 7

(C) 8

(D) 6

Homologous Series

→ Group of organic Comp having same Functional Group.
" " " " " Same chemical Reaction.
" " " " " Same chemical properties.
" " " " " Same General formula.

} But difference of "CH_2" Group or difference of Molecular wt 14.

CH_4	CH_3-OH	CH_3-NH_2
CH_3-CH_3	CH_3-CH_2-OH	$CH_3-CH_2-NH_2$
$CH_3-CH_2-CH_3$	$CH_3-CH_2-CH_2-OH$	$CH_3-CH_2-CH_2-NH_2$
$CH_3-CH_2-CH_2-CH_3$	$CH_3-CH_2-CH_2-CH_2-OH$	$CH_3-CH_2-CH_2-CH_2-NH_2$
$CH_3-CH_2-CH_2-CH_2-CH_3$	⋮	$CH_3-CH_2-CH_2-CH_2-CH_2-NH_2$
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$		⋮

Homologous Series

NOTE → Homologous Series have same chemical properties. → depends on FG.

→ Homologous series have different physical properties. → depends on Molecular wt.

→ Homologous Series के अंदर का एक Single comp को Homologue कहते हैं।

QUESTION:- The third member of the homologous series of aliphatic aldehyde has the structure:

(A) CH_3CH_2CHO

(B) $CH_3(CH_2)_2CHO$

(C) $CH_3COCH_2CH_3$

(D) CH_3COCH_3

1st mem → $H-\overset{O}{\overset{||}{C}}-H$

2nd mem → $CH_3-\overset{O}{\overset{||}{C}}-H$

3rd mem → $CH_3-CH_2-\overset{O}{\overset{||}{C}}-H$

$CH_3-\overset{O}{\overset{||}{C}}-CH_3$ ×

G15

N

5Ve⁻ → 3 bond → octet complete

aldehyde

$H/R-\overset{O}{\overset{||}{C}}-H$

$x = DU = 1$

$y = oxy = 1$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+2-2} \cdot O$

$C_nH_{2n} \cdot O$

$n = 3$

C_3H_6O

QUESTION:- The higher homologue of dimethyl ($CH_3 - NH - CH_3$) has the structure:

↓ 2° amine

(A) $CH_3 - N(CH_3) - CH_3$ 3° amine

(B) $CH_3 - CH_2 - CH_2 - NH_2$ 1° amine

(C) $CH_3 - NH - CH_2 - CH_3$ ✓

(D) $CH_3 - CH(NH_2) - CH_3$ 1° amine

$CH_3 - CH_2 - NH - CH_3$

QUESTION:- How many carbon atom are present in third homologue of dimethyl ether:

(A) 1

(B) 2

(C) 3

(D) 4 ✓

CH_3-O-CH_3 (1st)

$CH_3-CH_2-O-CH_3$ (2nd)

$CH_3-CH_2-CH_2-O-CH_3$ (3rd)

or

$CH_3-CH_2-O-CH_2-CH_3$

Note $\Longrightarrow$ 1° alcohol, 2° alcohol, 3° alcohol = belongs to same homologous series.

QUESTION:- Which of the following belongs to same Homologous series

(A) CH_3-CH_2-OH

(B) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$

(C) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

(D) all of these ✓

Same FG & "CH_2" difference → Homologous series

Note $\Longrightarrow$ 1° amine, 2° amine, 3° amine = do not belongs to same homologous series. Because functional group is different.

QUESTION:- Which of the following belongs to same Homologous series

(A) CH_3-NH_2 — 1° amine

(B) $CH_3-NH-CH_3$ — 2° amine

(C) $CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$ — 3° amine

(D) none of these ✓

different FG
↓
not homologous series.

QUESTION:- Which of the following belongs to same Homologous series

(A) $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ — 1° amide

(B) $CH_3-\overset{O}{\overset{\|}{C}}-NH-CH_3$ — 2° amide

(C) $CH_3-\overset{O}{\overset{\|}{C}}-N\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$ — 3° amide

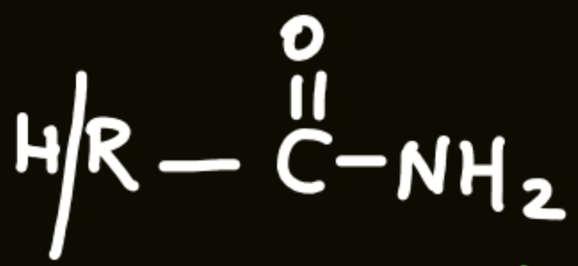
(D) none of these ✓

different FG } not Homologous series

Q Count num of Carbon in 9^{th} member of homologous series of i amide.

$\Rightarrow 9$

iamide



General Formula → $x = DU = 1$
$y = 1$ oxy $= 1$
$N = 1$

$C_nH_{2n+2-2x} \cdot O_y$

$C_nH_{2n+\cancel{2}-\cancel{2}} \cdot O_1 \cdot N$

$C_nH_{2n} \cdot O \cdot N$
$+1$

$C_nH_{2n+1} \cdot O \cdot N$

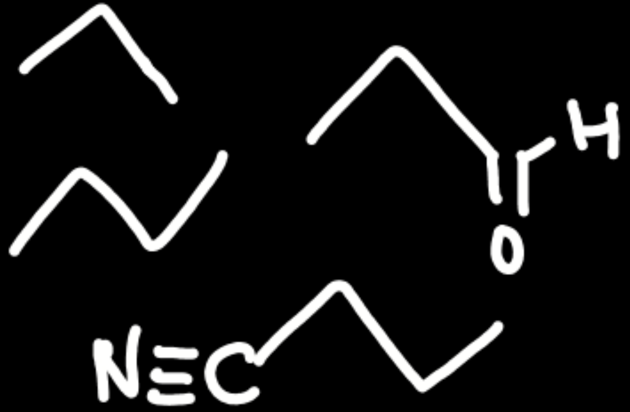
$n = 9$

$C_9H_{19} \cdot O \cdot N$

$C_9H_{17} \cdot O \cdot NH_2$

Classification of Organic compounds

- organic comp
  - Open chain comp: aliphatic, Acyclic
    - (wrt carbon) Saturated → (C–C) Single bond
    - Unsaturated → (C=C, C≡C) double/triple bond
  - Closed chain comp: Ring, cyclic
    - Homo cyclic (Carbocyclic) → Only carbon atom in cycle
      - Alicyclic
      - Aromatic
        - Benzenoid
        - non Benzenoid
    - Hetero cyclic → other than carbon atom in cycle
      - Alicyclic
      - Aromatic
        - Benzenoid
        - non Benzenoid





I will explain in next class (tomorrow) ↓ 10:00 am class

Classification of Organic compounds

Khaby Lame

Basic of organic

↓

FINISH

next chapter → IUPAC

↳ Tomorrow

10:00 am

Thank you
Future Doctors!!

NAMING OF ORGANIC COMPOUNDS

Common Naming or Trivial Naming	IUPAC Naming or Geneva Naming
1st part of Chapter	2nd part of Chapter

Trivial naming of organic compound

	Compound	Formula	Trivial name	Source/origin	popular name
1	Methane	CH_4	Marsh Gas	obtained from marshy places	methane
2	Methanol	CH_3-OH	wood spirit	obtained from destructive distillation of wood.	methanol
3	Urea	NH_2CONH_2	Urea	obtained from Urine.	Urea
4	Methanoic acid	$HCOOH$	Formic acid	Obtained from Formicus (Red Ant)	Formic acid
5	Ethanoic acid	CH_3-COOH	Acetic Acid	obtained from acetum (Vinegar)	acetic acid

Trivial naming of organic compound

S. No.	Formula	Trivial name	Source	Common Name
1	CH_4	Marsh gas	Obtained in (marsh by place)	Methane
2	NH_2CONH_2	Urea	Obtained from (Urine)	Urea
3	CH_3OH	Wood spirit	Obtained by (distractive distillation of wood	(Carbamide) Methyl alcohol
4	HCOOH	Formica	Obtained from formic us (Red ant)	Formic acid
5	CH_3COOH	Acetum	Obtained from Acetum (vinegar)	Acetic acid

Common Naming of Saturated Hydrocarbon

Name ⇒ Prefix + Word Root + Suffix → P+W+S

Word Root

→ Tells about num of carbon in organic Comp.

1 → meth	9 → non	17 → Heptadec	25 → Pentacos
2 → eth	10 → Dec	18 → octadec	26 → Hexacos
3 → prop	11 → Undec	19 → nonadec	27 → Heptacos
4 → But	12 → Dodec	20 → eicos/Icos	28 → octacos
5 → pent	13 → Tridec	21 → Heneicos	29 → nonacos
6 → Hex	14 → Tetradec	22 → docos	30 → Tricont
7 → Hept	15 → pentadec	23 → Tricos	40 → Tetracont
8 → oct	16 → Hexadec	24 → Tetracos	50 → pentacont
			100 → cent

Suffix & Prefix

Suffix

Tells about Saturation/unsaturation of an organic Comp.

C–C → ane

C=C → ene

C≡C → yne

Prefix

→ Tells about branching/unbranching in a comp.

used for unbranched OC (n → used for unbranched organic Comp. (n-prefix)

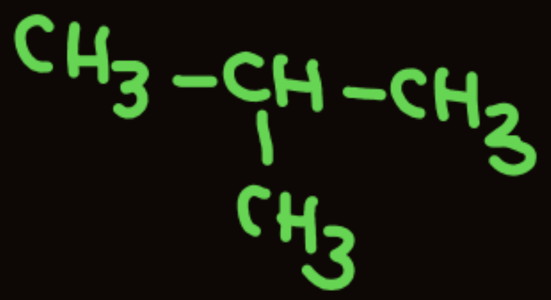
used for branched OC (
iso → used for branched OC → 2nd या 2nd last Carbon पर एक Carbon का branch है।
neo → " " " " → 2nd या 2nd last Carbon पर 2 अलग अलग Carbon का branch है।

Ex 1 CH_4 methane / marsh gas

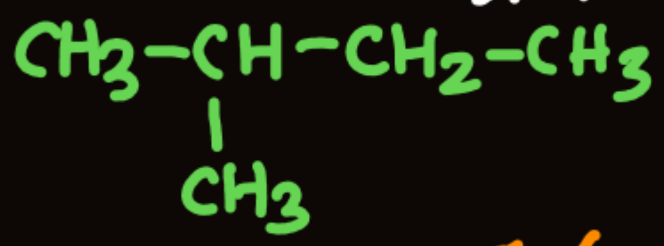
2 CH_3-CH_3 ethane

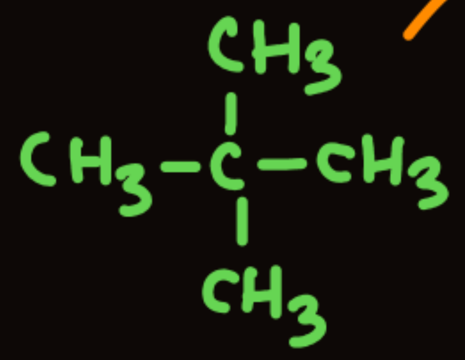
3 $CH_3-CH_2-CH_3$ propane

4 $CH_3-CH_2-CH_2-CH_3$ n-butane

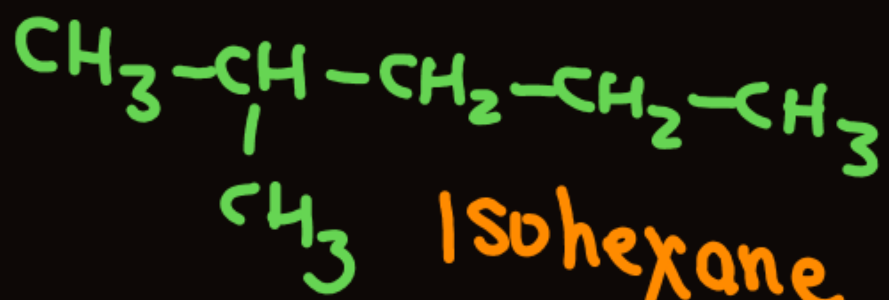
5  Isobutane

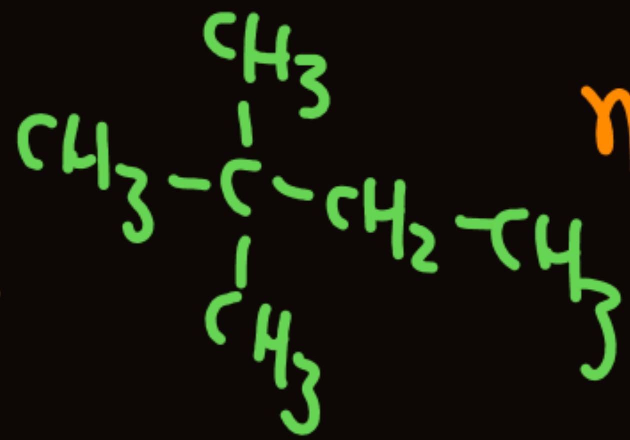
6 $CH_3-CH_2-CH_2-CH_2-CH_3$ n-pentane

7  Isopentane

8  Neopentane

9 $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ n-hexane

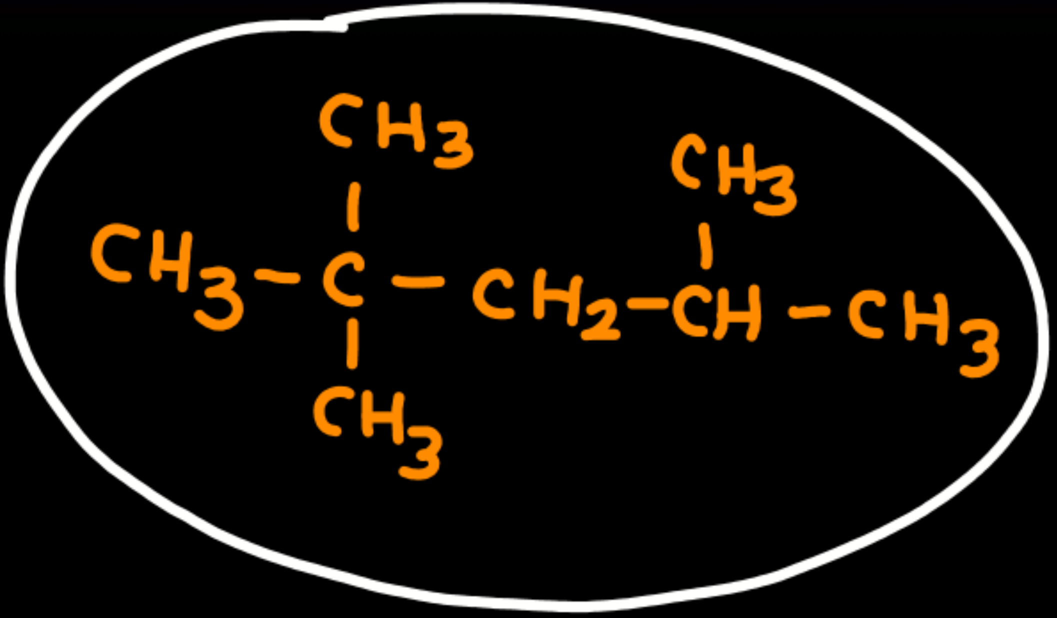
10  Isohexane

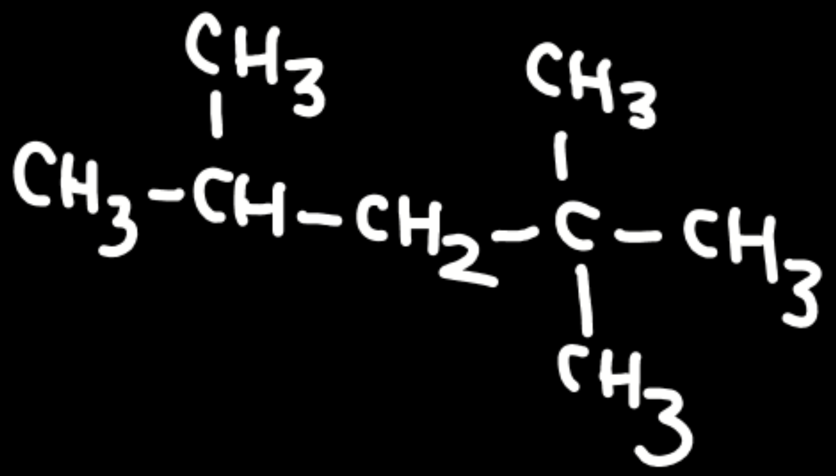
11  Neohexane

EXCEPTION

QUESTION:- Draw the structure of iso-octane:-

याद





Common naming of unsaturated Hydrocarbon

alkylene

olefenic bond → $C=C$ olefins

$C\equiv C$ acetylenes → acetylinic bond

$CH_2 = CH_2$ ⟶ ethylene

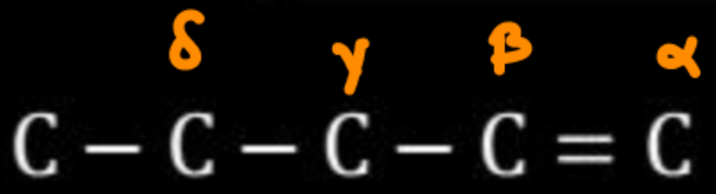
$CH_3 - CH = CH_2$ ⟶ propylene

$\overset{\delta}{C}H_3 - \overset{\gamma}{C}H_2 - \overset{\beta}{C}H = \overset{\alpha}{C}H_2$ ⟶ α-Butylene / n-α-Butylene

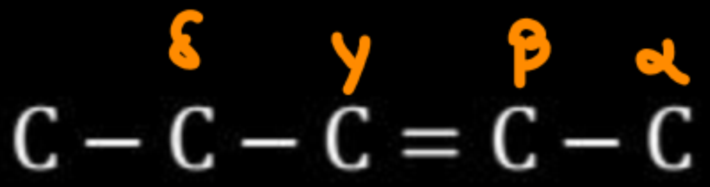
$\overset{\delta}{C}H_3 - \overset{\gamma}{C}H = \overset{\beta}{C}H - \overset{\alpha}{C}H_3$ ⟶ β-Butylene / n-β-Butylene

$CH_3 - C(CH_3) = CH_2$ ⟶ Isobutylene

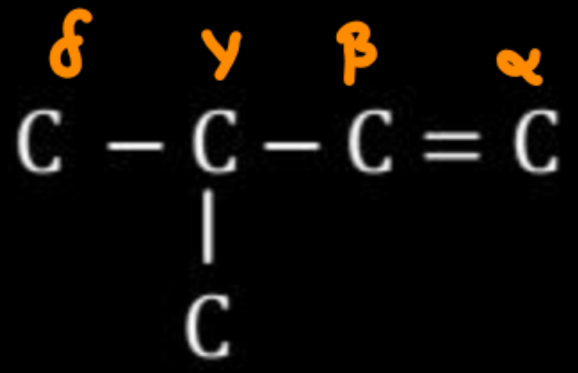
Common naming of unsaturated Hydrocarbon



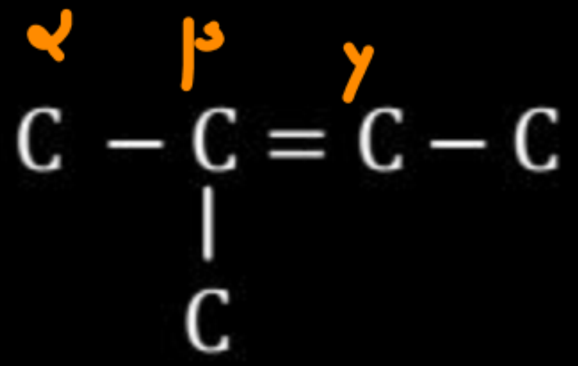
→ α-pentylene



→ β-pentylene



→ α-Isopentylene



→ β-Isopentylene

Common naming of unsaturated Hydrocarbon

$(C\equiv C)$ ⇒ common name ⇒ acetylene

$CH_3-CH_2-CH_2-C\equiv C-CH_3$ → Methyl propyl acetylene
(Propyl ... methyl)

$CH\equiv CH$ → Acetylene

$CH_3-C\equiv CH$ → Methyl acetylene

$CH_3-C\equiv C-CH_3$ → Dimethyl acetylene

$CH_3-CH_2-C\equiv C-CH_3$ → Ethyl Methyl acetylene
(ethyl ... methyl)

$CH_3-CH_2-CH_2-C\equiv C-CH_2-CH_3$
(Propyl ... Ethyl)
Ethyl propyl acetylene

$CH_3-CH_2-C\equiv C-CH_2-CH_3$
Diethyl acetylene

Thank you
Future Doctors!!

Suffix & Prefix

Prefix

① n prefix (normal) → used for unbranched (straight chain) organic comp.
→ used for organic comp having 4 or more carbo

② Iso prefix → used for branched organic comp.
→ When there is branch of one carbon at 2nd or 2nd last carbon in main chain.

③ Neo prefix → Used for branched organic comp.
→ When there is branch of two seperate carbon at 2nd or 2nd last carbon in main chain

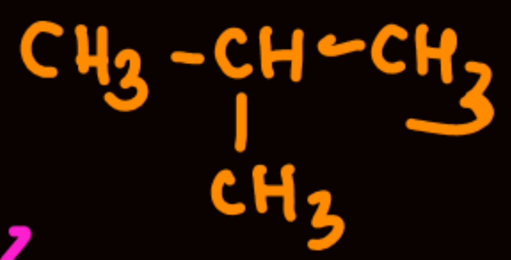
Ex

CH_4 → methane

CH_3-CH_3 → ethane

$CH_3-CH_2-CH_3$ → propane

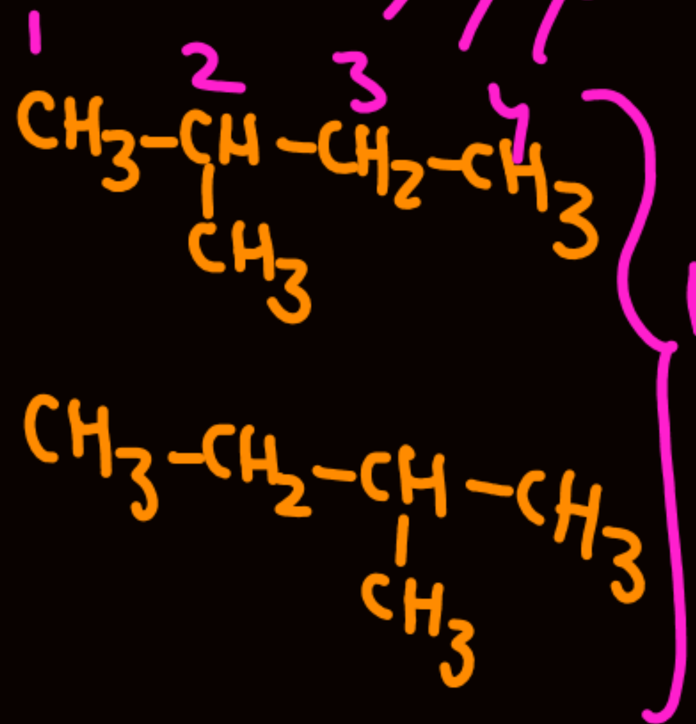
$CH_3-CH_2-CH_2-CH_3$ → n-butane



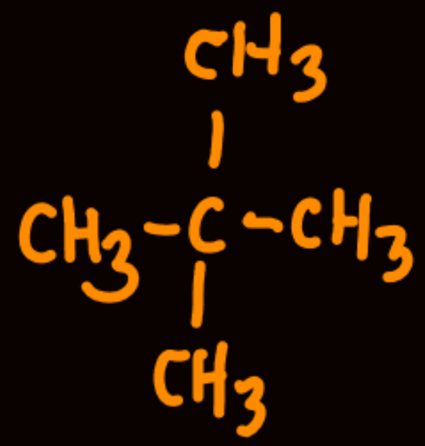
→ Isobutane

$CH_3-CH_2-CH_2-CH_2-CH_3$

n-pentane



Isopentane



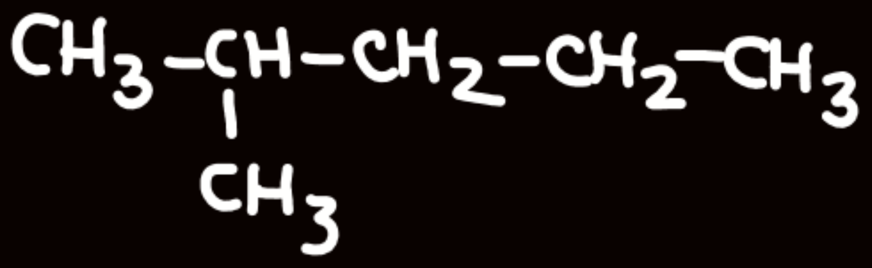
neopentane

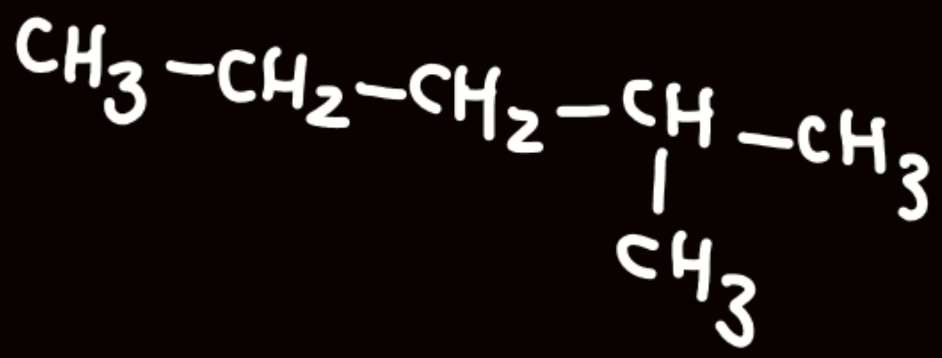
Que Draw the structure of n-hexane, Iso-hexane, neohexane —

n-hexane

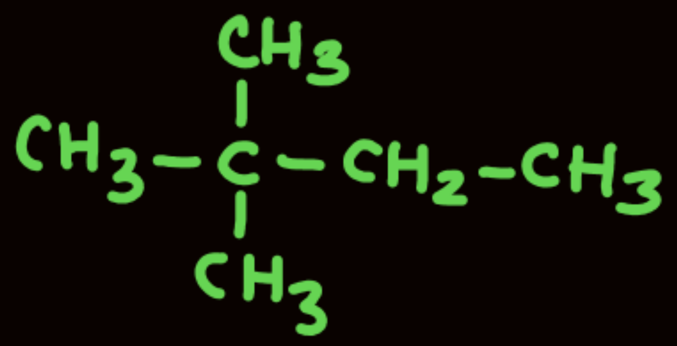
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

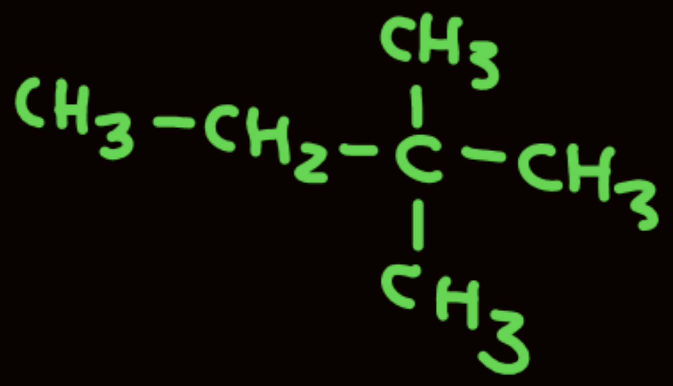
Iso-hexane

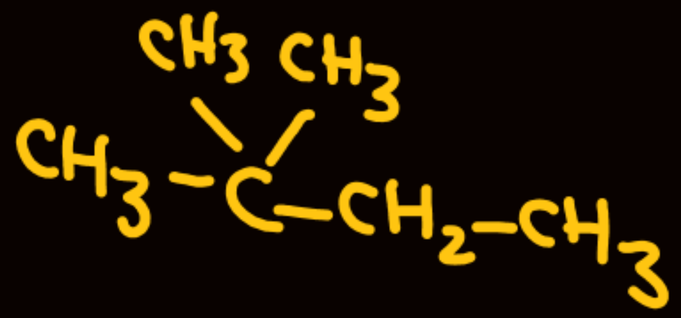




Neo-hexane

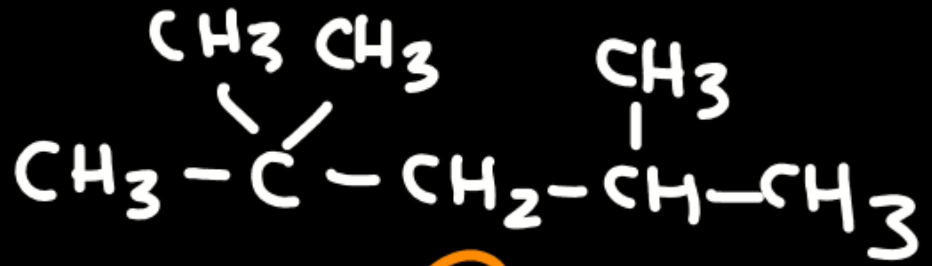




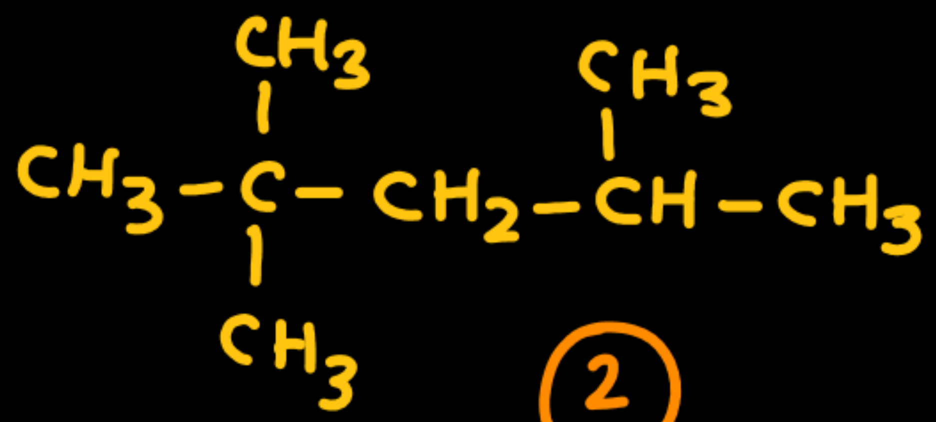


EXCEPTION याद

QUESTION:- Draw the structure of iso-octane:-

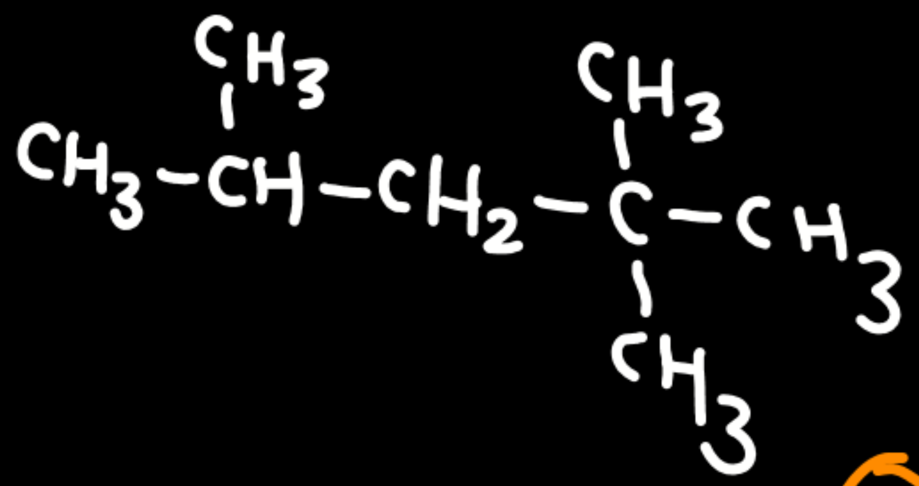


(1)



(2)

or



(3)

Common naming of unsaturated Hydrocarbon

Double bond → alkene → olefin (common name) → $>C=C<$ ⇒ Alkylene

note: "Alk" is used to represent wordroot in organic comp.

$CH_2 = CH_2$ ⟶ ethylene

$CH_3 - CH = CH_2$ ⟶ propylene

$\overset{\delta}{CH_3} - \overset{\gamma}{CH_2} - \overset{\beta}{CH} = \overset{\alpha}{CH_2}$ ⟶ α-Butylene

$\overset{\delta}{CH_3} - \overset{\gamma}{CH} = \overset{\beta}{CH} - \overset{\alpha}{CH_3}$ ⟶ β-Butylene

$CH_3 - C(CH_3) = CH_2$ ⟶ Iso-Butylene

note → There is only one compound of a single name.

Common naming of unsaturated Hydrocarbon

① $CH_3-\overset{\delta}{C}H_2-\overset{\gamma}{C}H_2-\overset{\beta}{C}H=\overset{\alpha}{C}H_2$ α-pentylene

② $CH_3-\overset{\delta}{C}H_2-\overset{\gamma}{C}H=\overset{\beta}{C}H-\overset{\alpha}{C}H_3$ β-pentylene

③ $\overset{\alpha}{C}H_3-\overset{\beta}{C}H=\overset{\gamma}{C}H-\overset{\delta}{C}H_2-CH_3$ β-pentylene

④ $\overset{\alpha}{C}H_2=\overset{\beta}{C}H-\overset{\gamma}{C}H_2-\overset{\delta}{C}H_2-CH_3$ α-pentylene

⑤ $\overset{\delta}{C}H_3-\overset{\gamma}{C}H(CH_3)-\overset{\beta}{C}H=\overset{\alpha}{C}H_2$ α-Isopentylene

⑥ $\overset{\alpha}{C}H_3-\overset{\beta}{C}(CH_3)=\overset{\gamma}{C}H-\overset{\delta}{C}H_3$ β-Isopentylene

Common naming of unsaturated Hydrocarbon

Alkyne → acetylenefamily → $-C\equiv C-$ ⇒ Acetylene

$CH\equiv CH$ ⟶ Acetylene

$CH_3 - C\equiv CH$ ⟶ Methyl acetylene

$CH_3 - C\equiv C - CH_3$ ⟶ Dimethyl acetylene

$CH_3 - CH_2 - C\equiv C - CH_3$ ⟶ Ethyl Methyl acetylen

Ethyl methyl

Common Naming of Radical

→ Compound formed after Removal of one or more Hydrogen is Called Radical.

Alkane

C_nH_{2n+2}

↓ −H

Alkyl (Radical)

C_nH_{2n+1}

Alkene

C_nH_{2n}

↓ −H

Alkenyl (Radical)

C_nH_{2n-1}

Alkyne

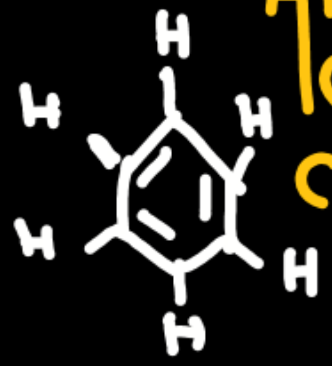
C_nH_{2n-2}

↓ −H

Alkynyl (Radical)

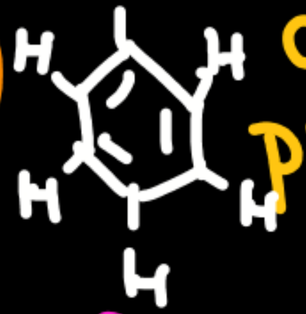
C_nH_{2n-3}

Arene (Benzene)



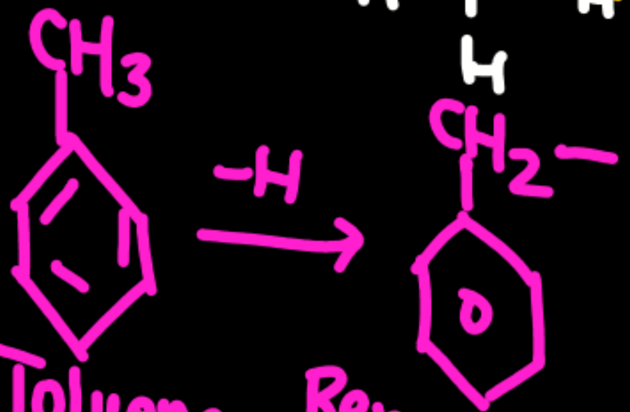
C_6H_6

↓ −H



C_6H_5

Phenyl



Toluene → Benzyl

Example

$CH_4 \xrightarrow{-H} CH_3-$

methane → methyl

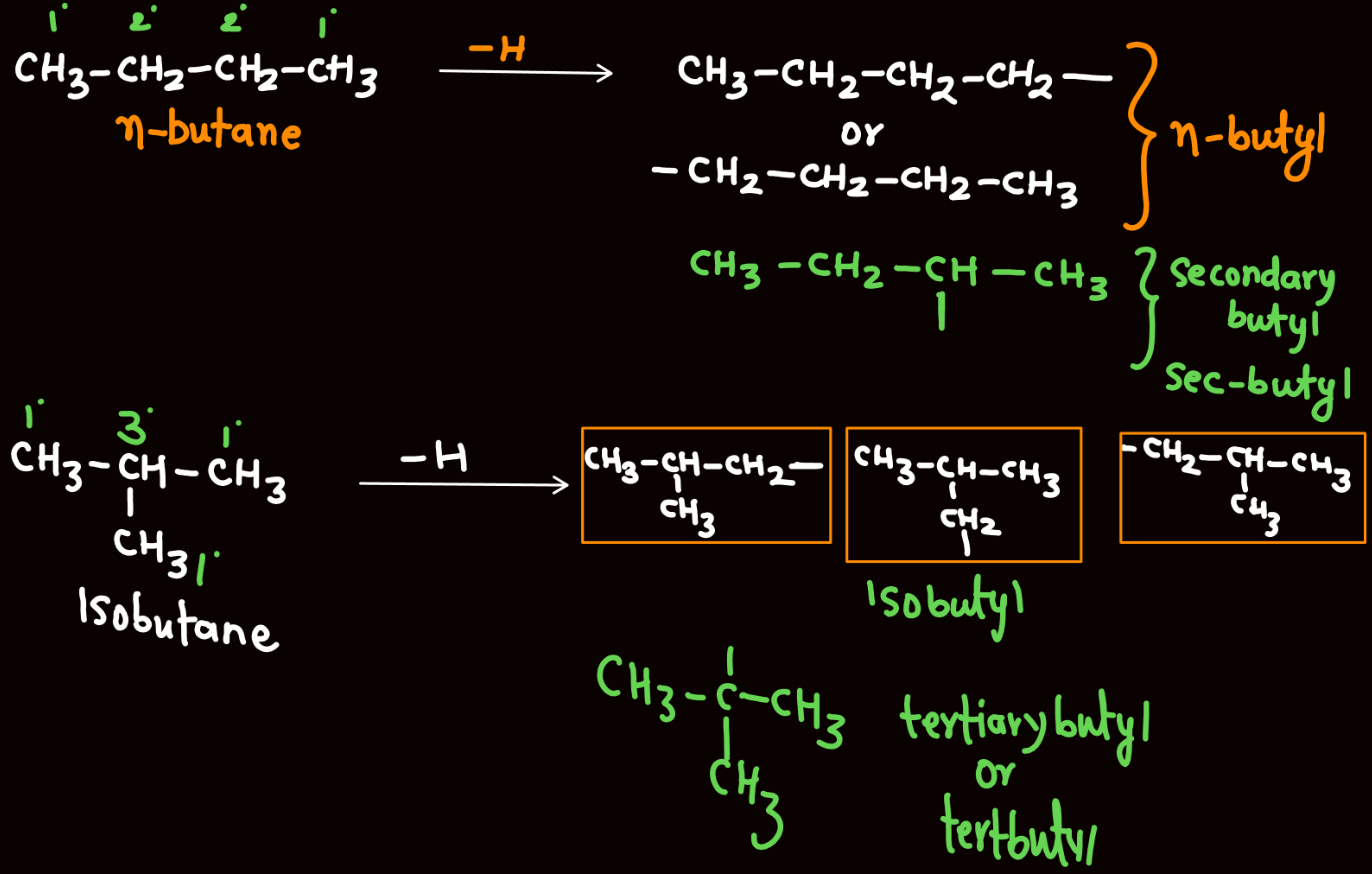
$CH_3-CH_3 \xrightarrow{-H} CH_3-CH_2-$ or $-CH_2-CH_3$

ethane → ethyl

$\overset{1^\circ}{CH_3}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3} \xrightarrow{-H} CH_3-CH_2-CH_2-$ or $-CH_2-CH_2-CH_3$

propane → propyl

(Exceptional) याद $CH_3-\underset{|}{CH}-CH_3$ Isopropyl



1° 2° 2° 1°
CH3-CH2-CH2-CH3
n-butane
-H
CH3-CH2-CH2-CH2—
or
—CH2-CH2-CH2-CH3
n-butyl
CH3-CH2-CH-CH3
Secondary butyl
Sec-butyl
1° 3° 1°
CH3-CH-CH3
CH3 1°
Isobutane
-H
CH3-CH-CH2—
CH3
CH3-CH-CH3
CH2
—CH2-CH-CH3
CH3
Isobutyl
CH3-C-CH3
CH3
tertiary butyl
or
tertbutyl

$\overset{1°}{CH_3}-\overset{2°}{CH_2}-\overset{2°}{CH_2}-\overset{2°}{CH_2}-\overset{1°}{CH_3}$

n-pentane

$\xrightarrow{-H}$ $CH_3-CH_2-CH_2-CH_2-CH_2-$

or

$-CH_2-CH_2-CH_2-CH_2-CH_3$

} n pentyl

<u>note</u> → Secpentyl / sechexyl ∴ donot exist

$CH_3-CH_2-CH_2-\underset{|}{CH}-CH_3$

$CH_3-CH_2-\underset{|}{CH}-CH_2-CH_3$

} X

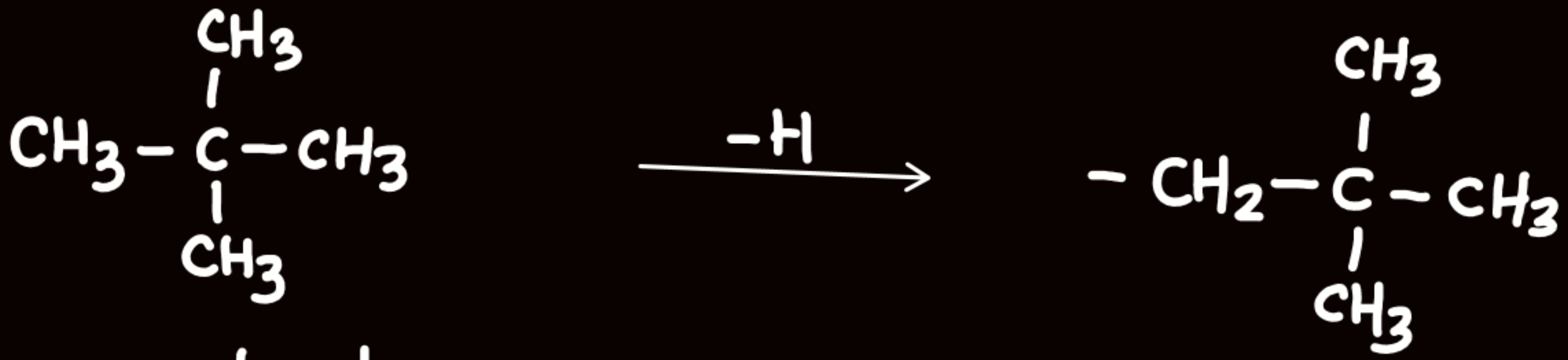
$\overset{1°}{CH_3}-\overset{3°}{CH}(\overset{1°}{CH_3})-\overset{2°}{CH_2}-\overset{1°}{CH_3}$ → $CH_3-CH(CH_3)-CH_2-CH_2-$ isopentyl

Isopentane

$CH_3-\overset{|}{C}(CH_3)-CH_2-CH_3$ tertiary pentyl

or

tert pentyl

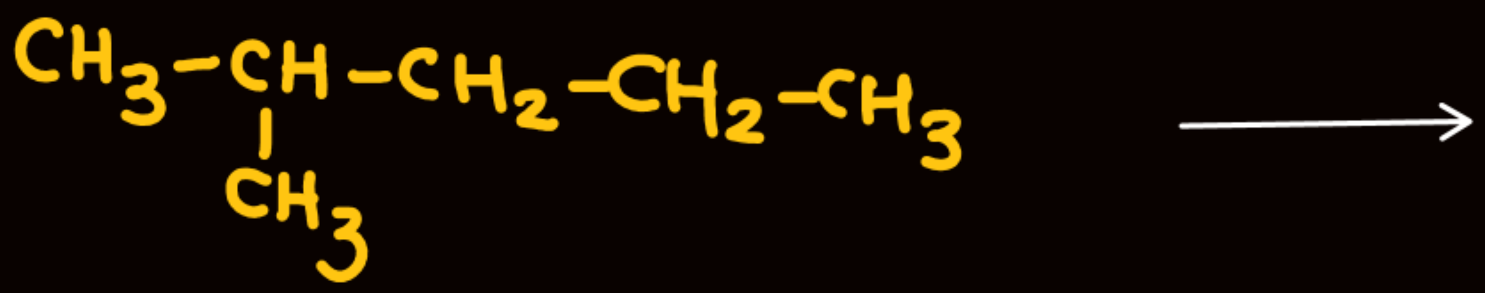


neopentane

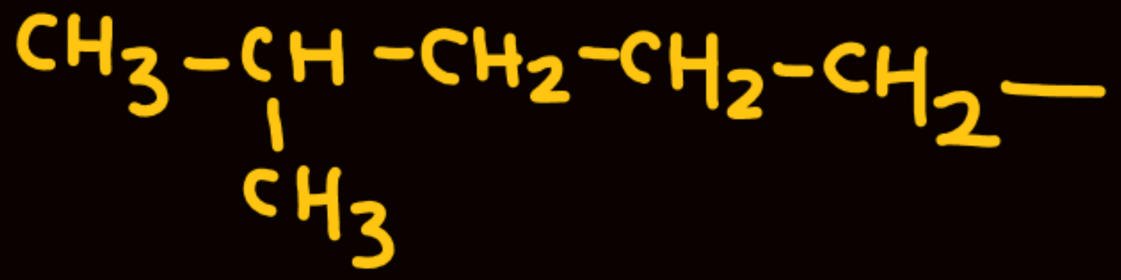
neopentyl

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \xrightarrow{-H} CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-$

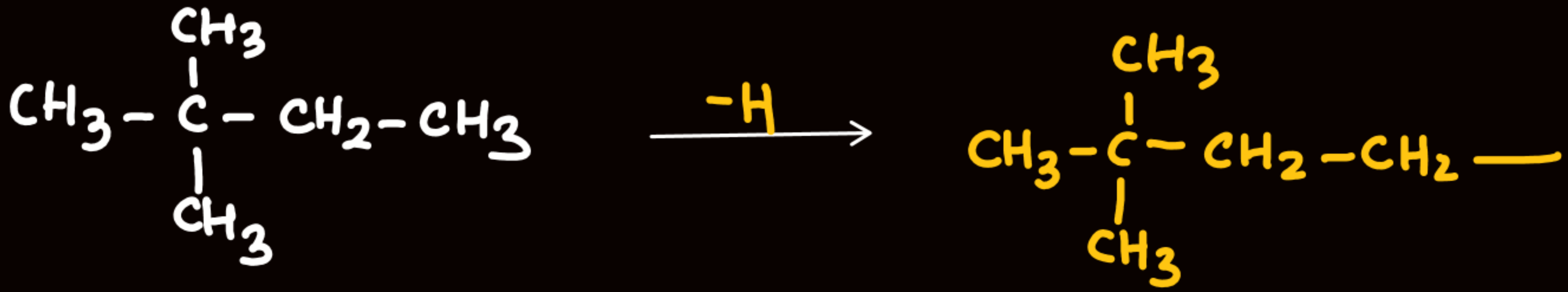
η-hexane → η-hexyl



Isohexane



Isohexyl



neohexane

neohexyl

THANK YOU

All the Best!! 👍

Recap

CH_4 methane $\xrightarrow{-H}$ $-CH_3$ methyl

CH_3-CH_3 ethane $\xrightarrow{-H}$ $-CH_2-CH_3$ ethyl

[1° 2° 1°] $CH_3-CH_2-CH_3$ propane $\xrightarrow{-H}$ $-CH_2-CH_2-CH_3$ propyl / n-propyl

Exception → $CH_3-CH(-)-CH_3$ Isopropyl

[1° 2° 2° 1°] $CH_3-CH_2-CH_2-CH_3$ n-Butane $\xrightarrow{-H}$ $-CH_2-CH_2-CH_2-CH_3$ n-butyl

$CH_3-CH(-)-CH_2-CH_3$ Secondary butyl / Sec-butyl

[1° 3° 1° 1°] $CH_3-CH(CH_3)-CH_3$ Isobutane $\xrightarrow{-H}$ $-CH_2-CH(CH_3)-CH_3$ isobutyl

$CH_3-C(-)(CH_3)-CH_3$ Tertiary butyl / Tert-butyl

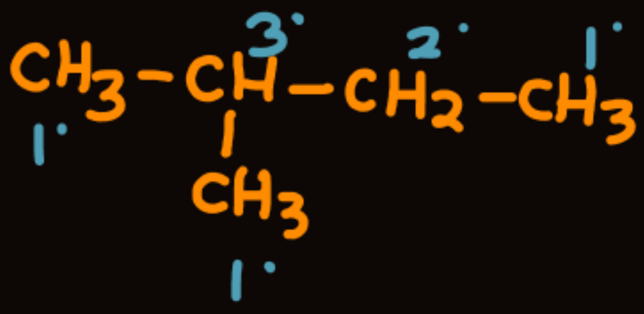
$\overset{1^\circ}{C}H_3-\overset{2^\circ}{C}H_2-\overset{2^\circ}{C}H_2-\overset{2^\circ}{C}H_2-\overset{1^\circ}{C}H_3$ n-pentane $\xrightarrow{-H}$ $-CH_2-CH_2-CH_2-CH_2-CH_3$

n-pentyl

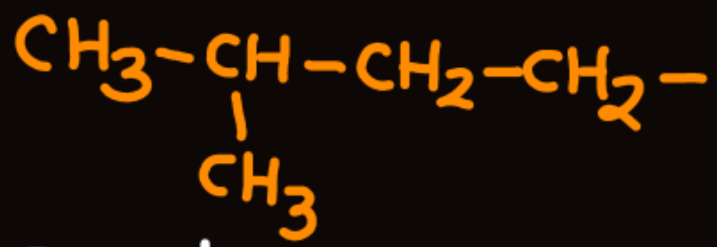
NOTE → Sec pentyl, Sec-hexyl, Sec heptyl...... donot exist.

X { $CH_3-\underset{|}{C}H-CH_2-CH_2-CH_3$ Sec pentyl

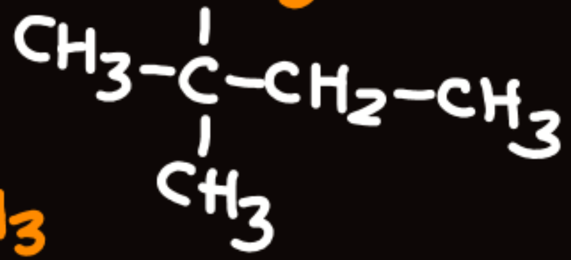
$CH_3-CH_2-\underset{|}{C}H-CH_2-CH_3$ Sec pentyl }



Isopentane $\xrightarrow{-H}$

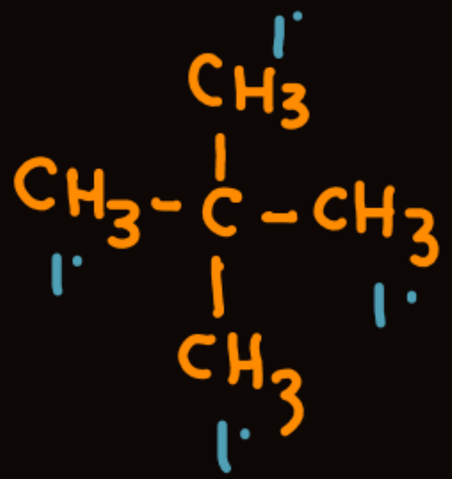


Isopentyl

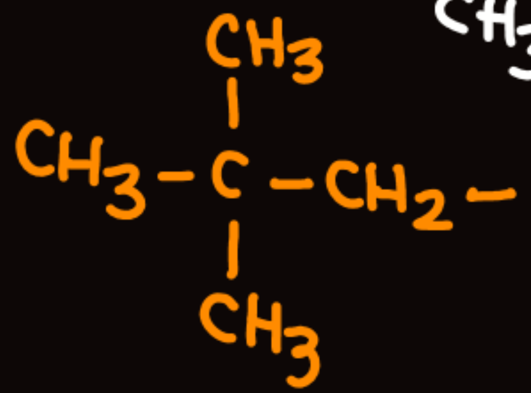


Tertiary pentyl

Tert pentyl



neo pentane $\xrightarrow{-H}$



neopentyl

$$\underset{\text{n-hexane}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3} \xrightarrow{-H} \underset{\text{n-hexyl}}{-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3}$$

$$\underset{\text{Iso-hexane}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3} \xrightarrow{-H} \underset{\text{Isohexyl}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-}$$

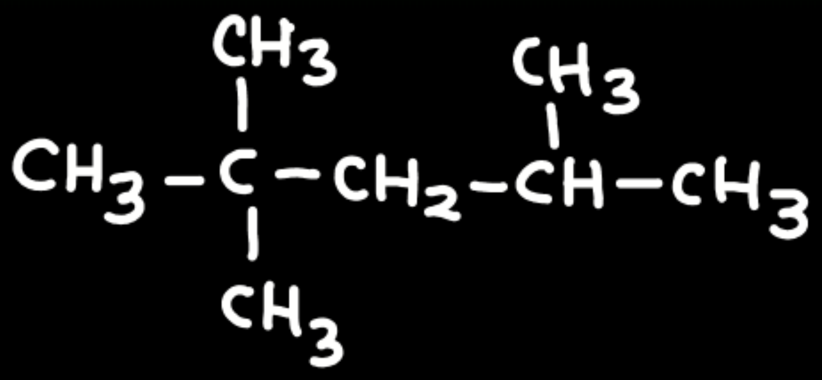
$$\xrightarrow{-H} CH_3-\underset{\underset{CH_3}{|}}{\overset{|}{C}}-CH_2-CH_2-CH_3 \quad \text{Tertiaryhexyl}$$

Tert hexyl

$$\underset{\text{neohexane}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3} \xrightarrow{-H} \underset{\text{Neohexyl}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-}$$

QUESTION:- Draw the structure of iso-octane:-

Exception



Iso-octane

Common naming of Bivalent Radical

C−C−C−C (bonds on the first two carbons): Vicinal position

C−C−C−C< (two bonds on one carbon): geminal

Bivalent Radical

Geminal — Alkylidene

2H is released from same carbon

↓

$CH_4 \xrightarrow{-2H} CH_2<$ methylidene

$CH_3-CH_3 \xrightarrow{-2H} CH_3-CH<$ ethylidene

$CH_3-CH_2-CH_3 \xrightarrow{-2H} CH_3-CH_2-CH<$ Propylidene

Bivalent Radical

Vicinal — Alkylene

2 H is from neighbouring Carbon

$CH_3-CH_3 \xrightarrow{-2H} -CH_2-CH_2-$ ethylene

$CH_3-CH_2-CH_3 \xrightarrow{-2H} -CH_2-CH(-)-CH_3$ Propylene

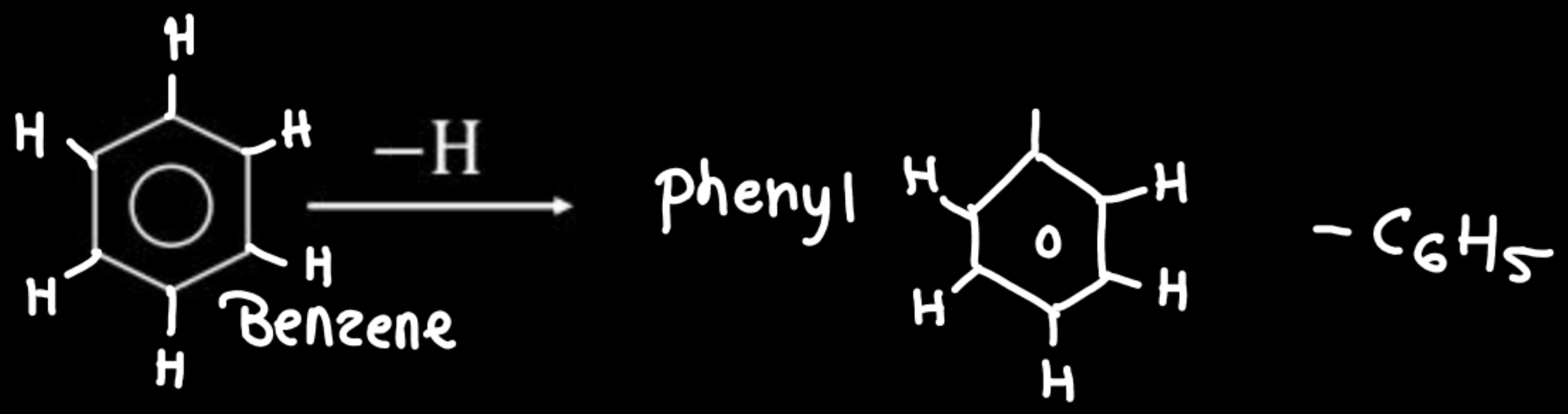
Trivalent Radical (Alkylidyne)

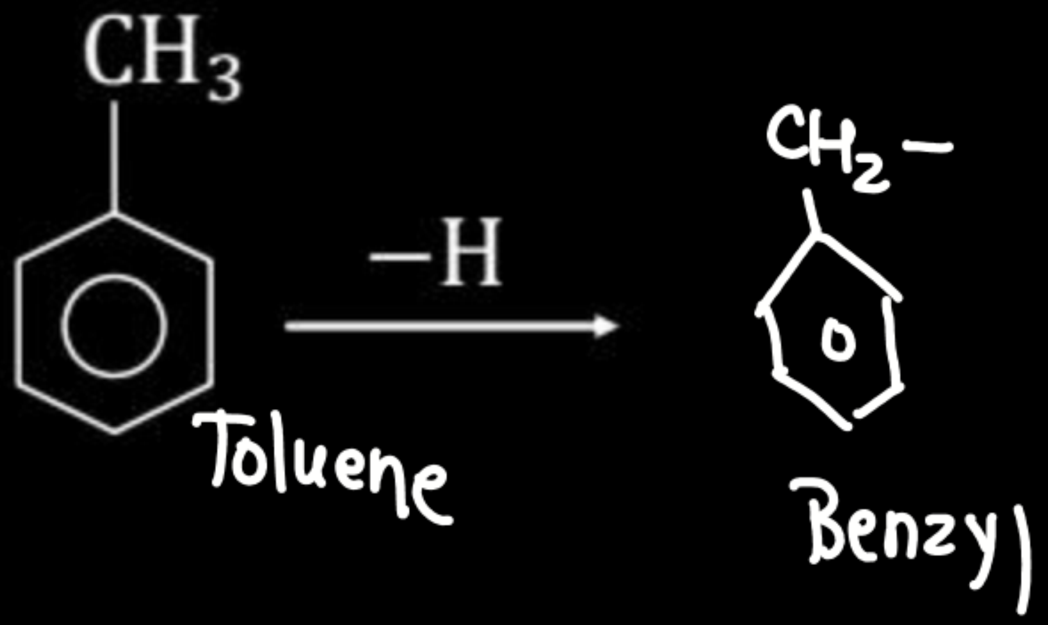
$CH_4 \xrightarrow{-3H} CH\equiv$ methylidyne

$CH_3-CH_3 \xrightarrow{-3H} CH_3-C\equiv$ ethylidyne

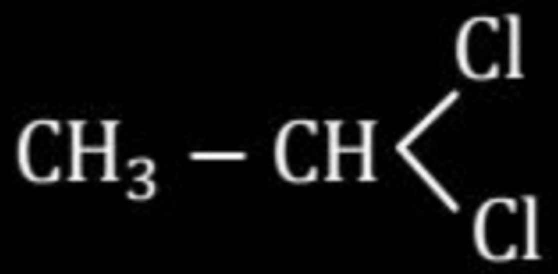
$CH_3-CH_2-CH_3 \xrightarrow{-3H} CH_3-CH_2-C\equiv$ Propylidyne

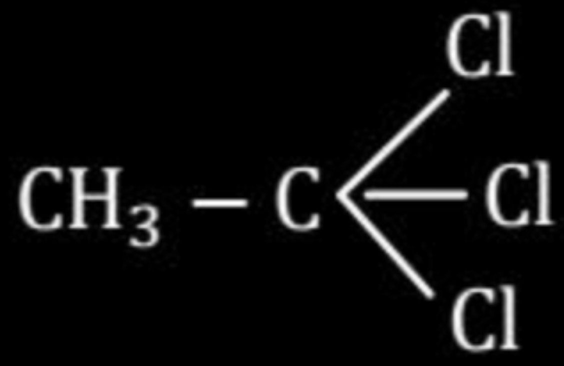
Common naming of Aromatic Hydrocarbon

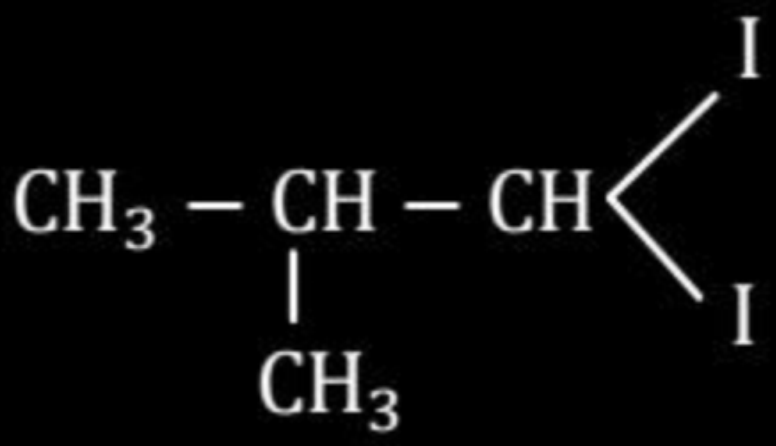


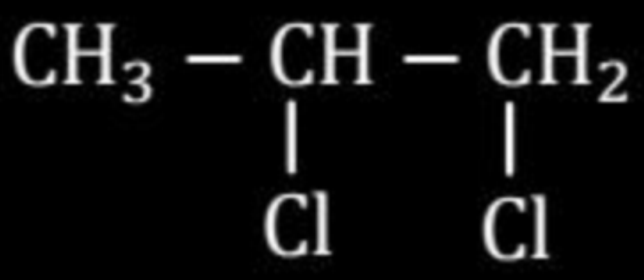


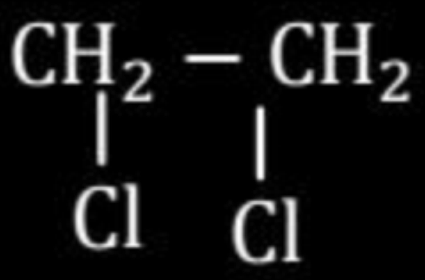
QUESTION:- **Write the common name of following organic compounds:**

I.  ⟶ ethylidene chloride

II.  ⟶ ethylidyne chloride

III.  → Isobutylidene Iodide

IV.  → Propylene Chloride

V.  → Ethylene chloride

Common naming with Functional Group

Num of Carbon → Common name

1 → Form

2 → Acet

3 → Propion

4 → Butyr

5 → Valer

C=C–C– → Acryl

C–C=C–C– → Croton

Common naming Of Organic Compound

Function Group		Suffix
$-C(=O)-H$	⟶	aldehyde
$-C(=O)-OH$	⟶	ic acid
$-C(=O)-O\underline{R}$	⟶	Alkyl ……. ate
$-C(=O)-O-C(=O)-$	⟶	ic anhydride

↳ word Root a/c to common name

Common naming of Organic Compound

Function Group	Suffix
$-\overset{O}{\overset{\Vert}{C}}-X$ →	yl halide
$-\overset{O}{\overset{\Vert}{C}}-NH_2$ →	amide
$-C\equiv N$ →	o nitrile
$-N\equiv C$ →	o isonitrile

Common naming of Organic Compound

$HCHO$	$\longrightarrow$	Formaldehyde
CH_3-CHO	$\longrightarrow$	Acetaldehyde
CH_3CH_2CHO	$\longrightarrow$	propionaldehyde
$CH_3CH_2CH_2CHO$	$\longrightarrow$	Butyraldehyde
$CH_3CH_2CH_2CH_2CHO$	$\longrightarrow$	Valeraldehyde
$CH_2=CH-CHO$	$\longrightarrow$	Acrylaldehyde
$CH_3-CH=CH-CHO$	$\longrightarrow$	crotonaldehyde

Common naming of Organic Compound

$HCOOH$ ⟶ Formic acid

CH_3COOH ⟶ Acetic acid

CH_3CH_2COOH ⟶ Propionic acid

$CH_3CH_2CH_2COOH$ ⟶ Butyric acid

$CH_3(CH_2)_3COOH$ ⟶ Valeric acid

$CH_2 = CH - COOH$ ⟶ Acrylic acid

$CH_3 - CH = CH - COOH$
↓
Crotonic acid

Common naming of Organic Compound

$CH_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH=CH-CH_3$

Ethyl Crotonate

$H-\overset{O}{\overset{\|}{C}}-O-CH_3$ ⟶ Methyl Formate

$CH_3-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ ↓ Methyl propionate

$CH_3-\underset{CH_3}{\underset{|}{CH}}-O-\overset{O}{\overset{\|}{C}}-CH_3$ ⟶ Isopropyl Acetate

$CH_3-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$

Methyl Butyrate

$CH_2=CH-\overset{O}{\overset{\|}{C}}-O-C_2H_5$ ⟶ Ethyl Acrylate

$CH_3-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_3$

Methyl Valerate

Common naming of Organic Compound

$$\underbrace{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}}_{\text{Acet}}-O-\underbrace{\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}_{\text{Acet}} \longrightarrow \text{Acetic anhydride}$$

$$\underbrace{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}}_{\text{Acet}}-O-\underbrace{\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3}_{\text{Propion}} \longrightarrow \text{Acetic propionic anhydride}$$

Common naming of Organic Compound

$H-\overset{\overset{O}{||}}{C}-Cl \longrightarrow$ Formyl chloride

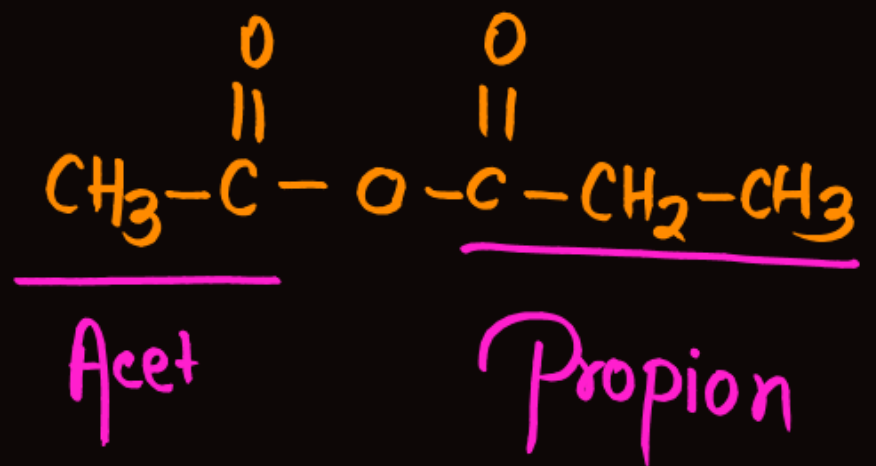
$CH_3-\overset{\overset{O}{||}}{C}-Cl \longrightarrow$ Acetyl chloride

$C_2H_5-\overset{\overset{O}{||}}{C}-Cl \longrightarrow$ propionyl chloride

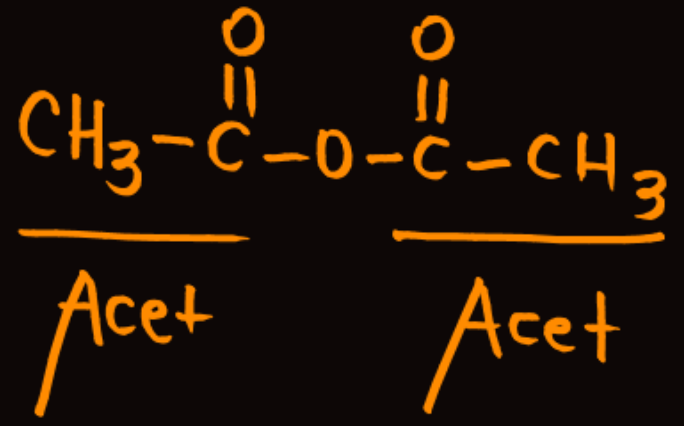
$C_3H_7-\overset{\overset{O}{||}}{C}-Cl \longrightarrow$ Butyryl chloride

Common naming of Organic Compound

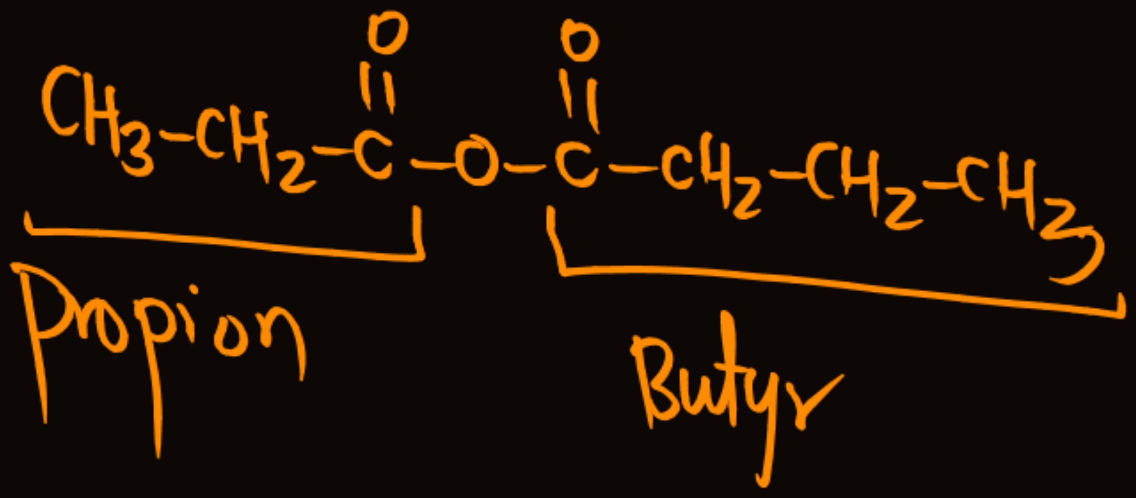
$H-\overset{\overset{\displaystyle O}{\|\|}}{C}-NH_2$	Formamide
$CH_3-\overset{\overset{\displaystyle O}{\|\|}}{C}-NH_2$	Acetamide
$C_2H_5-\overset{\overset{\displaystyle O}{\|\|}}{C}-NH_2$	Propionamide
CH_3-CN	Acetonitrile
CH_3-CH_2-CN	Propiononitrile
$CH_3-N\equiv C$	Acetoisonitrile



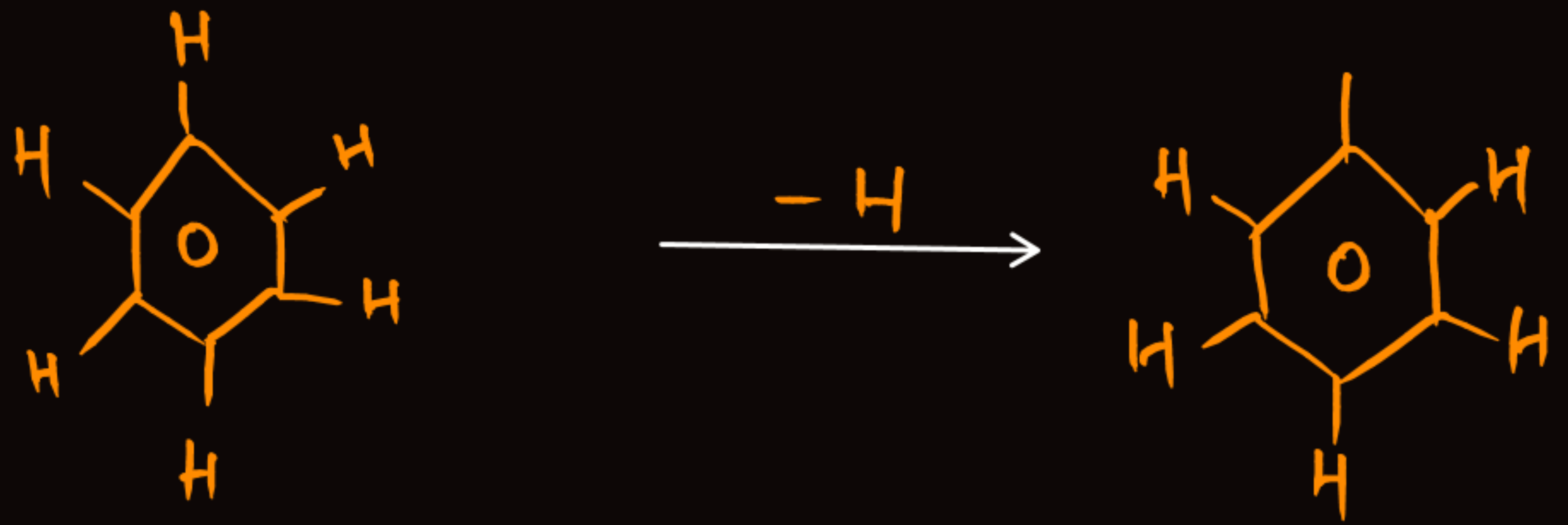
Acetic Propionic anhydride



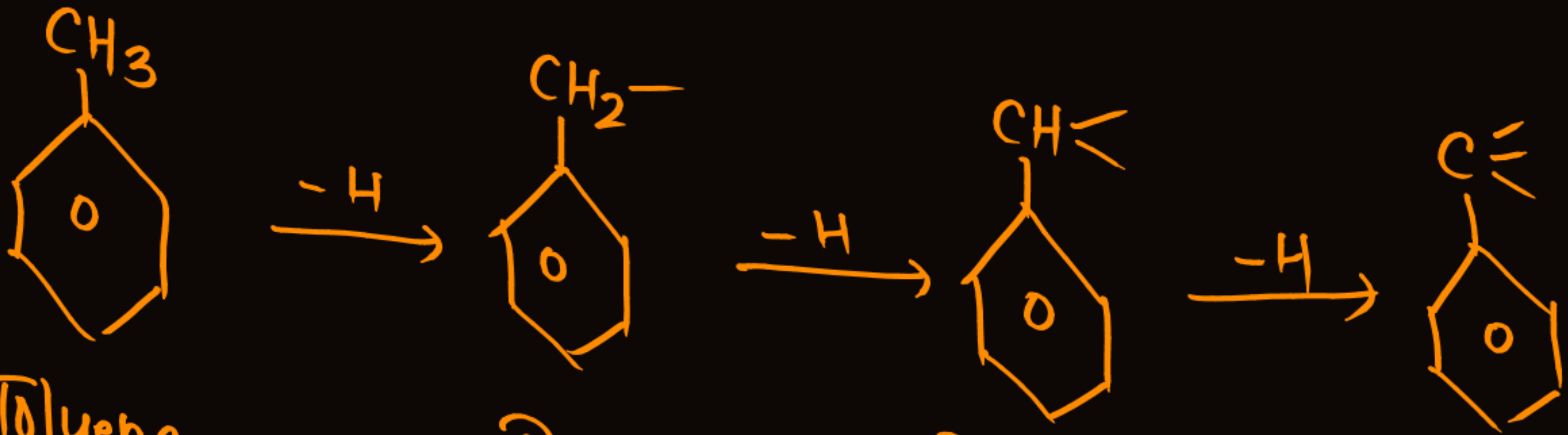
Aceticanhydride



ButyricPropionic anhydride



Benzene C_6H_6 → Phenyl $-C_6H_5$



Toluene → Benzyl → Benzylidene (Benzal) → Benzylidyne (Benzo)

THANK YOU

All the Best!! 👍

Lecture-1

IUPAC Nomenclature of organic Comp

IUPAC Nomenclature = Prefix + wordroot + suffix

= 2° Prefix + 1° Prefix + wordroot + 1° suffix + 2° suffix

= 21012

Syllabus

Wordroot

↳ Tells about num of Carbon in organic Comp.

1 → meth	11 → Undec	21 → Heneicos
2 → eth	12 → Dodec	⋮
3 → prop	13 → Tridec	30 → Tricont
4 → But	14 → Tetradec	40 → Tetracont
5 → pent	15 → pentadec	50 → pentacont
6 → Hex	16 → Hexadec	60 → Hexacont
7 → Hept	17 → Heptadec	70 → Heptacont
8 → Oct	18 → Octadec	⋮
9 → Non	19 → nonadec	100 → Cent
10 → Dec	20 → EIcos/ICOS	

Prefix

2' Prefix

Tells about Sidechain/Branch/Substituent in organic comp.

- $-X$ → Halo
- $-F$ → Fluro
- $-Cl$ → Chloro
- $-Br$ → Bromo
- $-I$ → Iodo
- $-NO_2$ → Nitro
- $-ONO$ → Nitrite
- $-NO$ → Nitroso
- $-NH_2$ → Amino
- $-R$ → Alkyl
- $-CH_3$ → methyl
- $-CH_2-CH_3$ → ethyl

$-CH_2-CH_2-CH_3$ propyl

$CH_3-\overset{|}{C}H-CH_3$ isopropyl

$-CH_2-CH_2-CH_2-CH_3$ n-butyl

$CH_3-\overset{|}{C}H-CH_2-CH_3$ Sec-butyl

$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-$ Isobutyl

$CH_3-O-CH_2-CH_3$ → AlkoxyAlkane (छोटा, बड़ा)

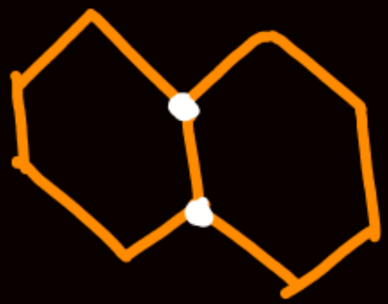
Methoxyethane

1' Prefix

Tells about the Compound whether it is closed chain or not.



→ Cyclo



→ Bicyclo (2 Bridge head Carbon)



→ Spiro (1 Bridge head Carbon)

Suffix

\# Vowel → a, e, i, o, u

\# di, tri, tetra is never used in alphabatical Rule.

1' suffix

Tells about saturation/unsaturation in a Comp.

C–C → ane

C=C → ene

C≡C → yne

C=C–C=C → diene

C≡C–C≡C → diyne

C=C–C=C–C=C → triene

C≡C–C≡C–C≡C → triyne

C=C–C≡C → enéyne → enyne

C=C–C≡C–C=C → dieneyne → dienyne

C≡C–C=C–C≡C → enediyne

2' suffix

Tells about functional group in a Comp.

–COOH → oic acid

$-SO_3H$ → Sulphonic acid

–CHO → al

–OH → ol

–CO– → one

$-CONH_2$ → amide

–COX → oyl halide

–COBr → oyl Bromide

–COCl → oyl chloride

note → while writing Suffix.

Last letter of one Suffix and first letter of other Suffix.

⇓

Can't be "two Vowel"

&

Can't be a "Vowel and a y".

↓

Cancel the former Vowel.

Example:

$CH_4 \longrightarrow$ Methane

$CH_3-CH_3 \longrightarrow$ Ethane

$CH_3-CH_2-CH_3 \longrightarrow$ Propane

$CH_3-CH_2-CH_2-CH_3 \longrightarrow$ Butane

$CH_2=CH_2 \longrightarrow$ Ethene

$CH_3-CH=CH_2 \longrightarrow$ propene

$CH\equiv CH \longrightarrow$ Ethyne

$CH_3-C\equiv CH \longrightarrow$ Propyne

$\underset{1}{CH_3}-\underset{2}{CH}=\underset{3}{CH}-\underset{4}{CH}=\underset{5}{CH}-\underset{6}{CH_3} \longrightarrow$ Hexa-2,4-diene

$\underset{1}{CH_3}-\underset{2}{C}\equiv\underset{3}{C}-\underset{4}{C}\equiv\underset{5}{C}-\underset{6}{CH_3} \longrightarrow$ Hexa-2,4-diyne

note → when more than one double bond or more than one triple bond is present then (wordroot + a) is used.

ALKa

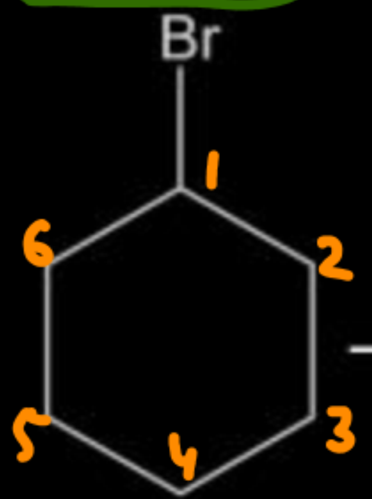
Examples:

CH_3CH_2Br → 1-Bromoethane / Bromoethane

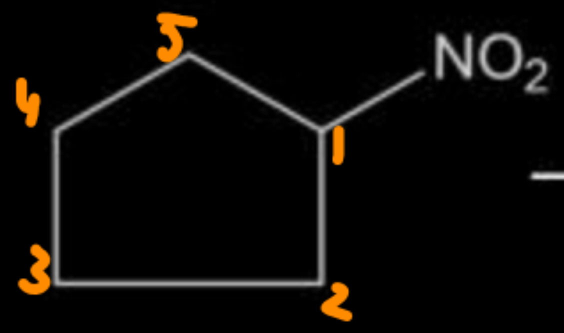
CH_3NO_2 → 1-nitromethane / Nitromethane

$C_2H_5 - O - C_2H_5$ → Ethoxyethane

$CH_3 - O - C_2H_5$ → Methoxyethane



→ 1-Bromocyclohexane / Bromocyclohexane



→ 1-nitrocyclopentane / nitrocyclopentane

R-O-R

Small Carbon → alkoxy

More no of Carbon → alkane

Alkoxy Alkane

IUPAC Nomenclature of Saturated Organic Comp

⇓ Comp containing only Single bond.

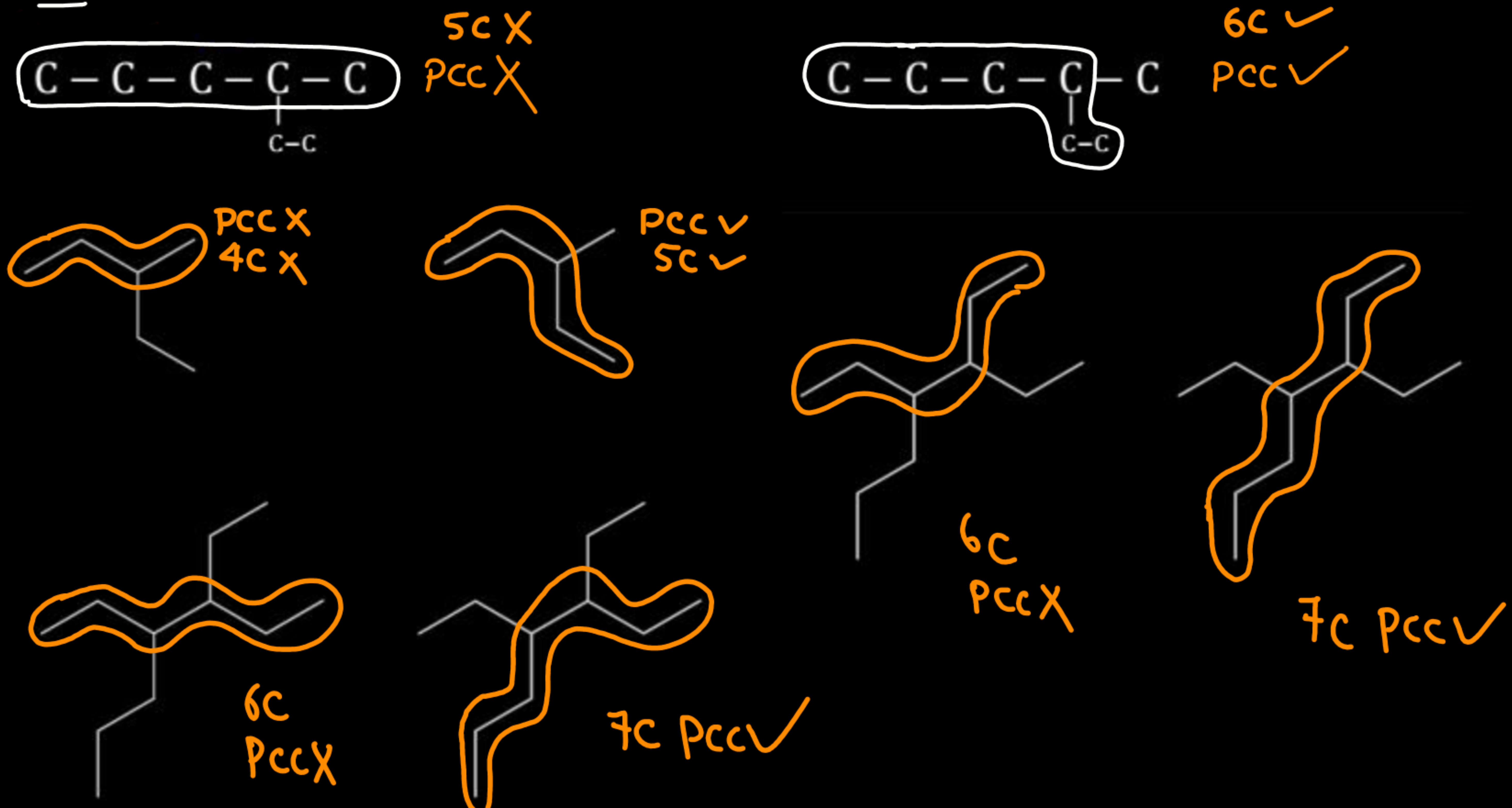
P.C.C.

Rule 1 → Selection of Parent Carbon chain / Main Chain / Principle chain

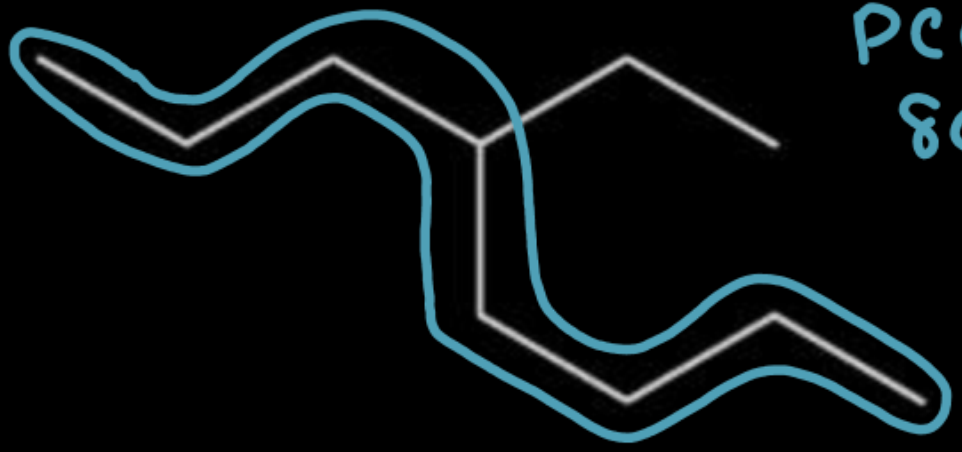
\# Select that carbon chain Which has maximum number of Carbon.

Rules of IUPAC Nomenclature

Ex

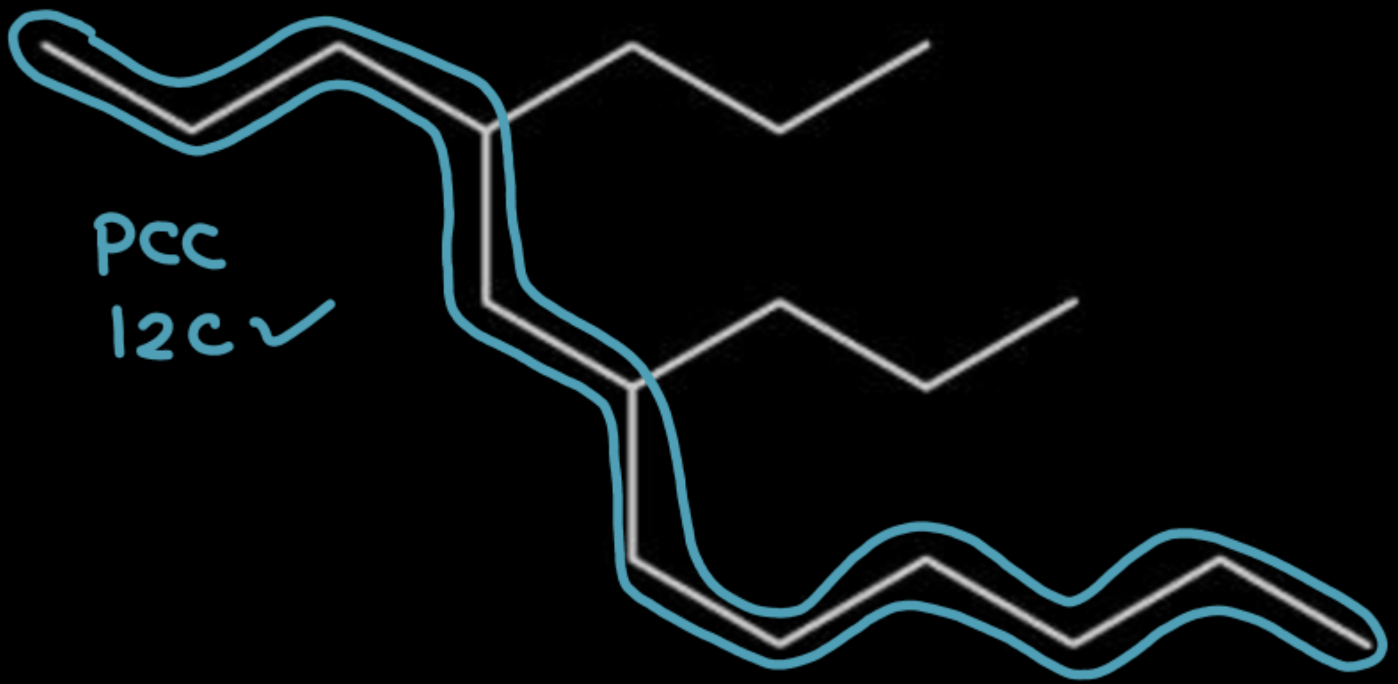


Select the PCC in the following compounds:



PCC
8C ✓

Q2



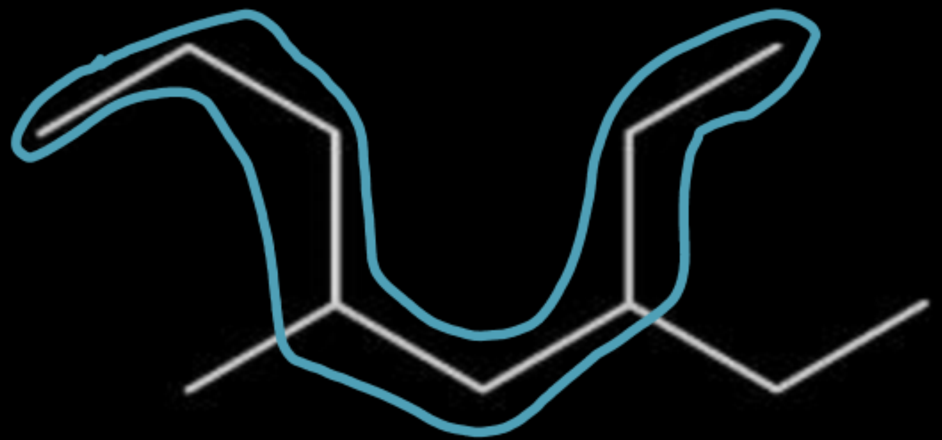
PCC
12C ✓

Q3



PCC
9C ✓

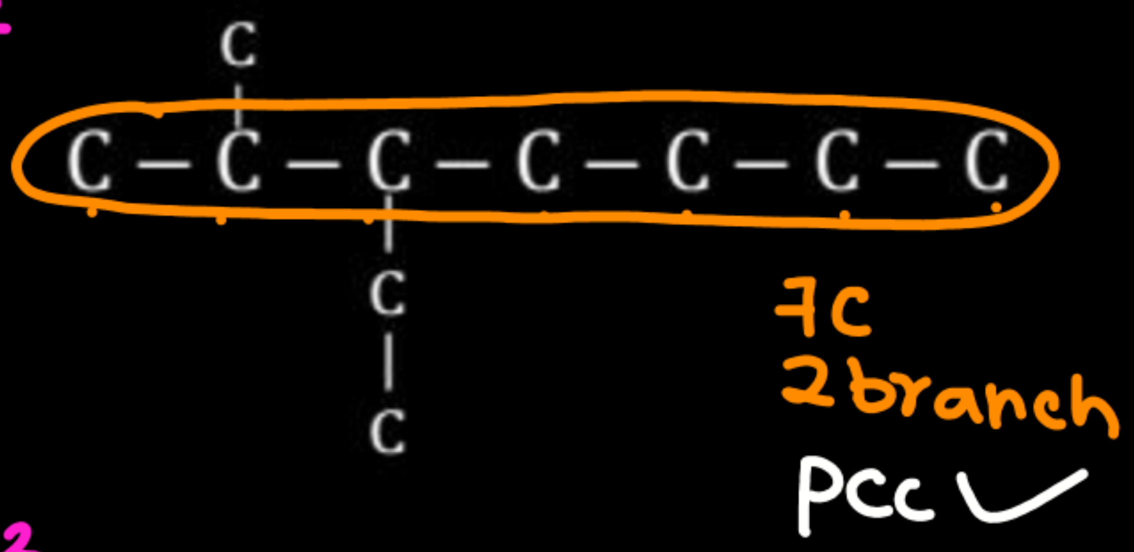
Q4

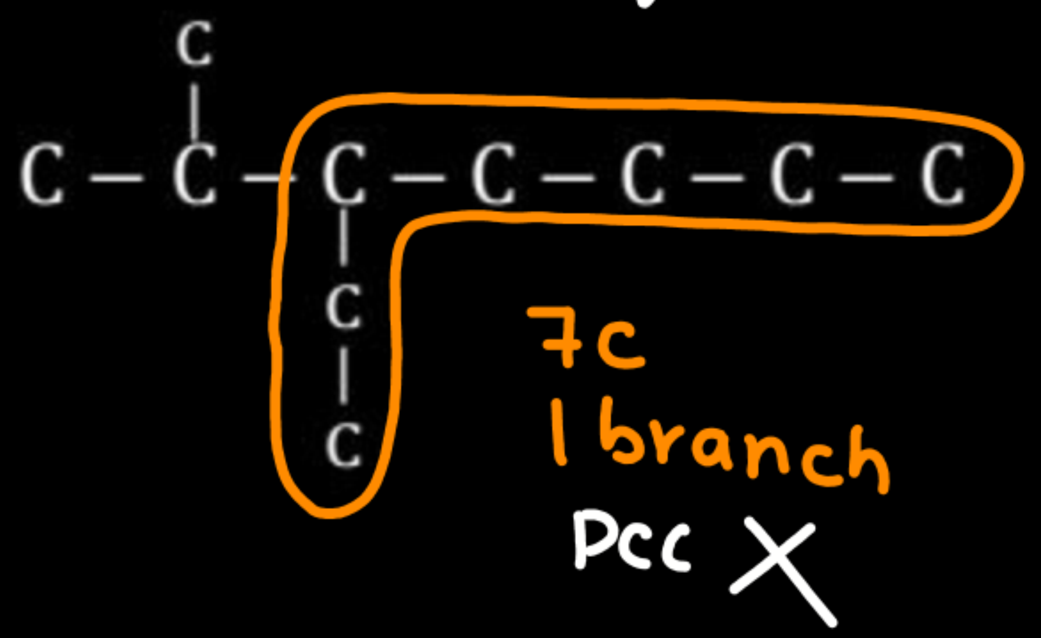


Rule 2 : In case of more than one carbon chain having same number of carbon

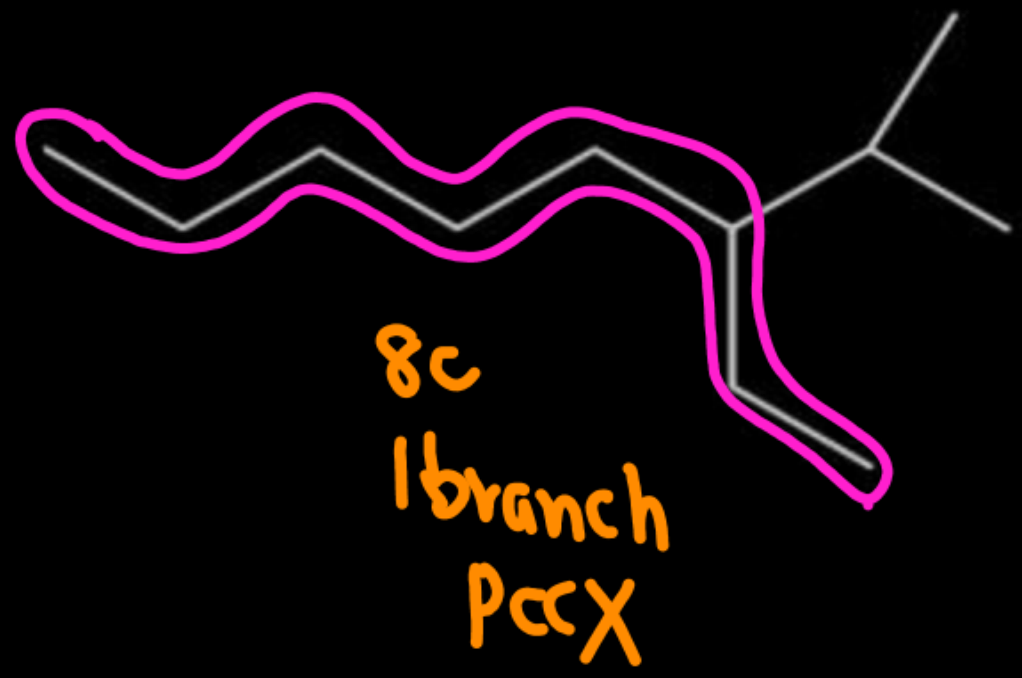
Final PCC will be that carbon chain which has max num of carbon as well as max branch.

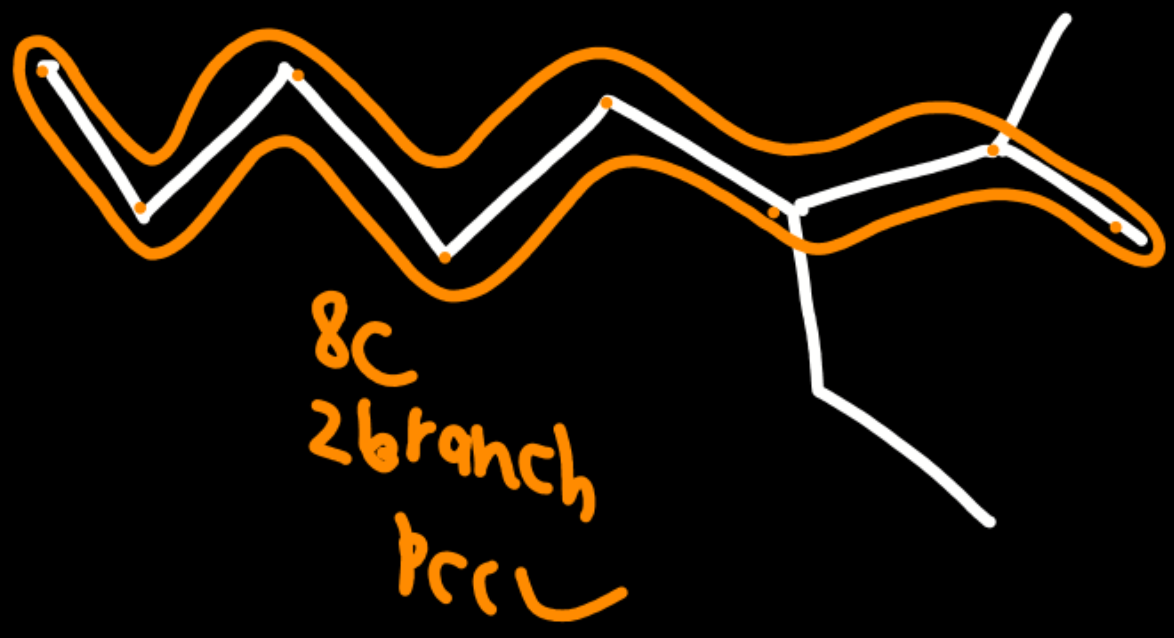
Q1



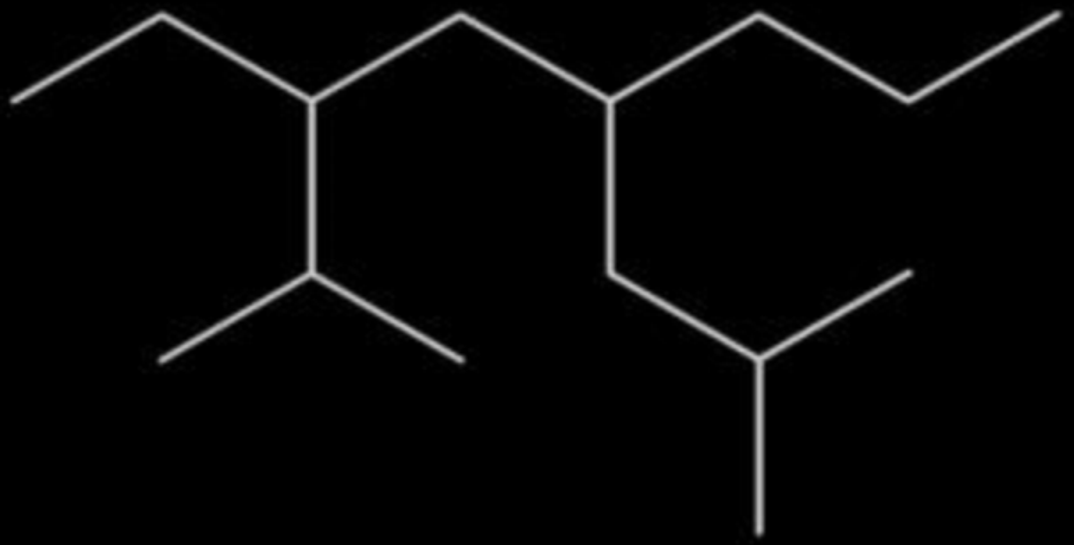


Q2

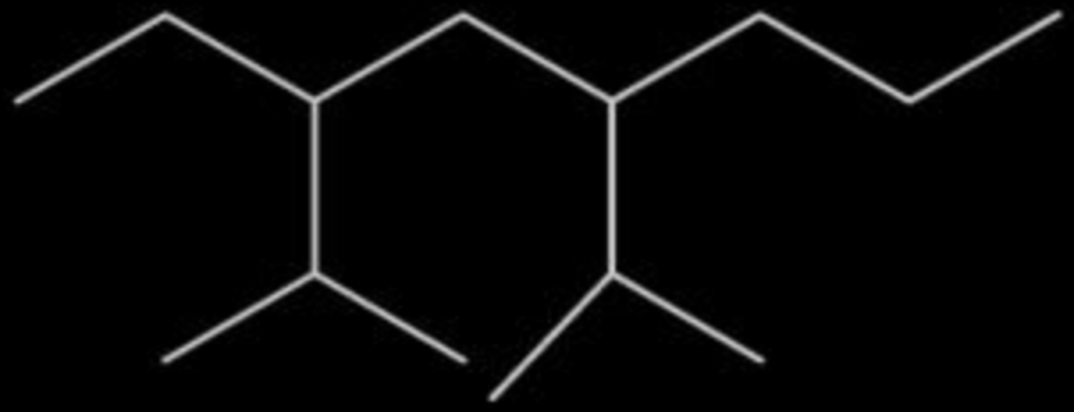




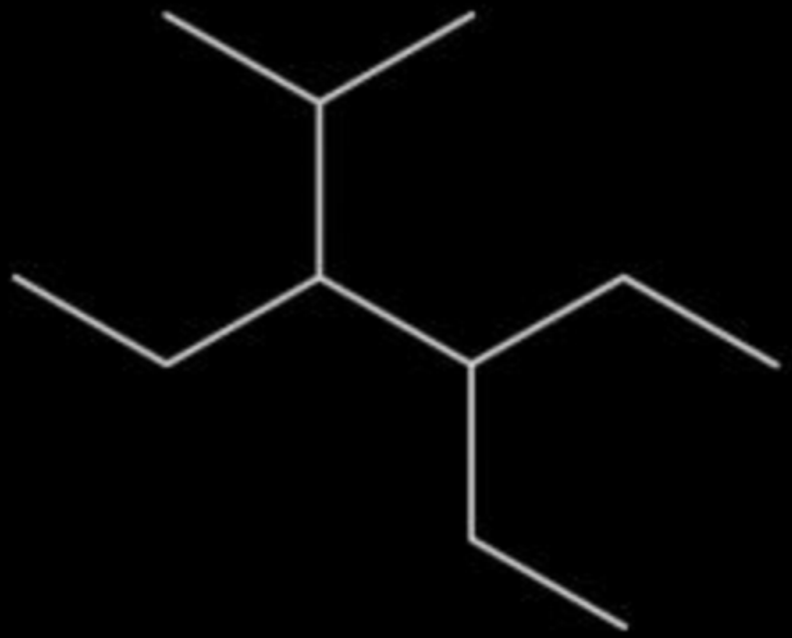
Q3



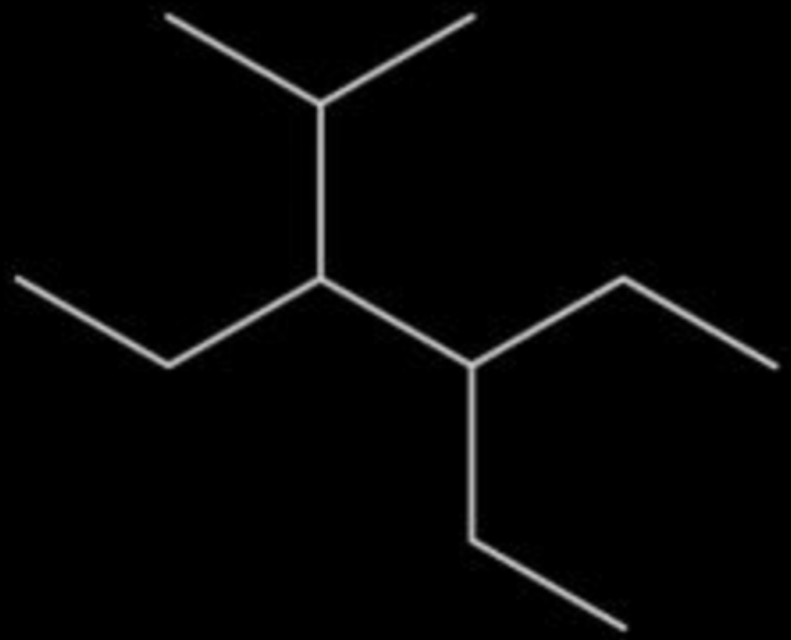
Q4



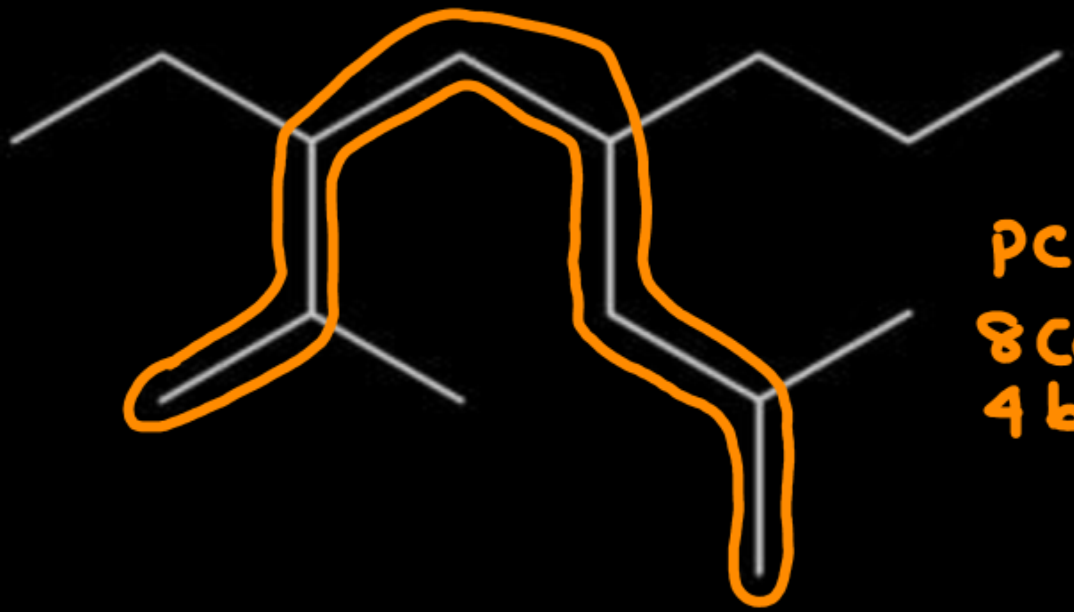
Q5



Q6

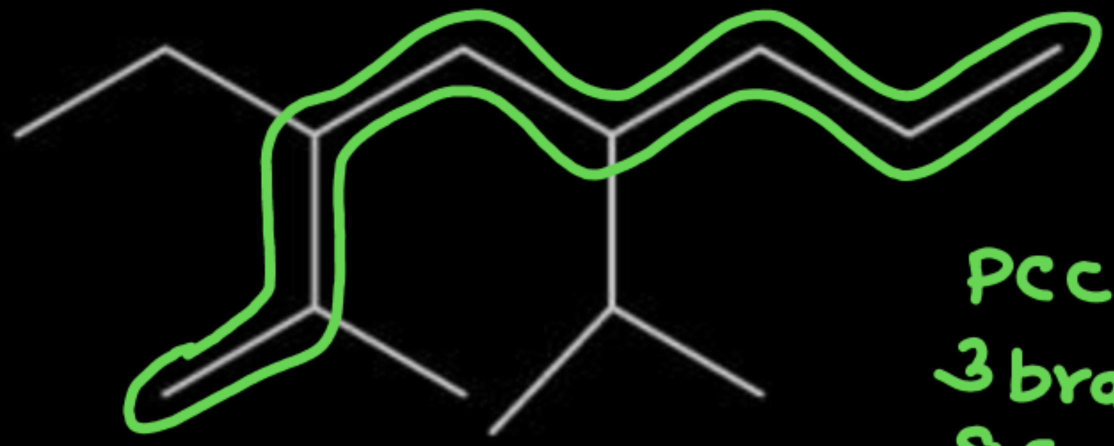


Rule (selection of PCC) → ① Max no of Carbon ② Max num of Branch



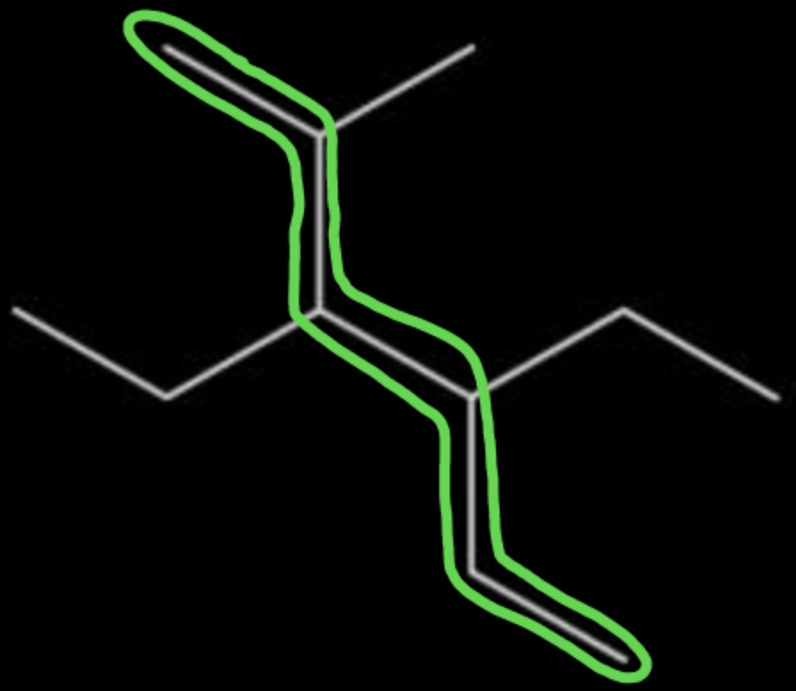
PCC ✓
8 Carbon
4 branch

Q2



PCC ✓
3 branch ✓
8 Carbon

Q3



PCC ✓
6 C
3 branch

IUPAC Naming of Saturated Organic Comp

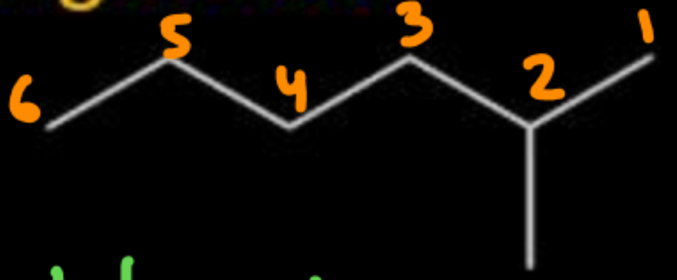
Rule 1 Selection $\xrightarrow{PCC}$
1. Max num of Carbon
2. Max num of Branch

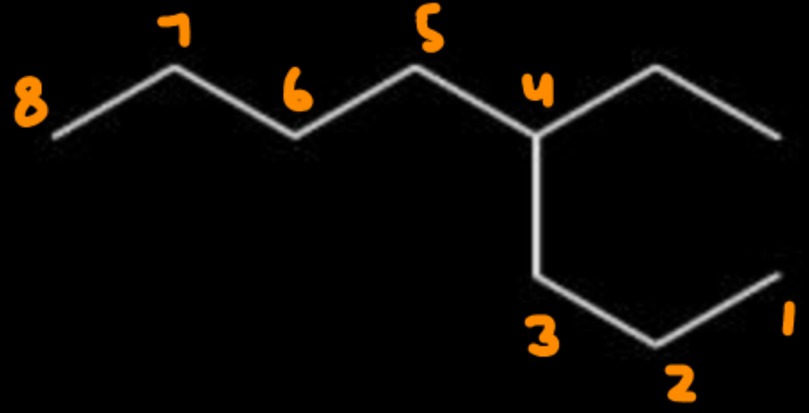
Rule 2 Numbering $\xrightarrow{PCC}$
1. Lowest Locant Rule (→ Single branch) → Lowest Num is given to branch.
2. Lowest Locant Sum Rule (→ Multiple branch) → Sum of all locant num should be small.
3. Alphatical Rule → If Sum rule fails then numbering is done in alphabatical manner.

Rule 3 Naming $\xrightarrow{PCC}$
1. Always follow 2 1 0 1 2 → 2°P → 1°P → WR → 1°S → 2°S
2. Incase of more than one 2° Prefix / 1° suffix → Follow alphatical Rule.
3. In case of more than one same 2° Prefix or same 1° suffix: 2 → di, 3 → tri, 4 → tetra
4. Di/Tri/Tetra is not used in alphabatical order.
5. Iso/neo is used in alphabatical order.
6. In IUPAC name → two digits are separated by Comma (,)
7. Digits & alphabet is separated by Hyphen (—)
8. There is no space/gap in IUPAC name.

Numbering of PCC:

Lowest Locant → Rule ↳ Single branch





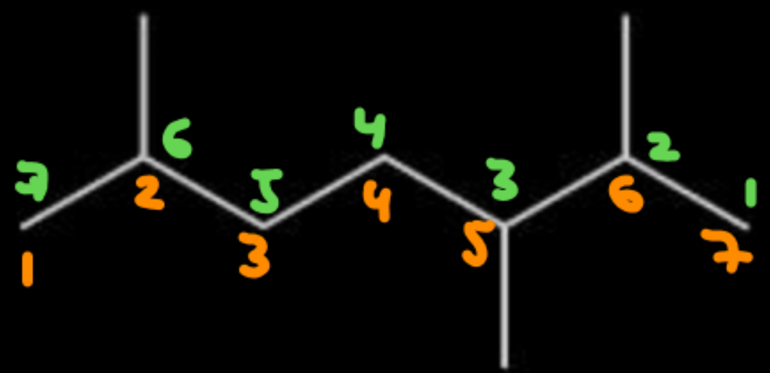


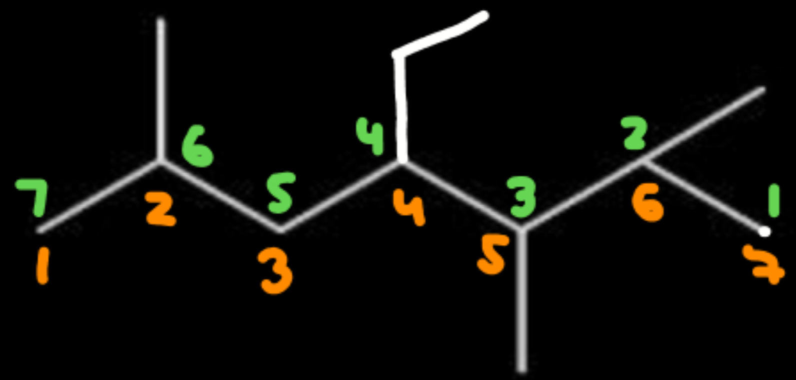
ethyl

✓ L → 3,5,5,7
✗ R → 3,5,5,7
} alphabetical Rule

methyl

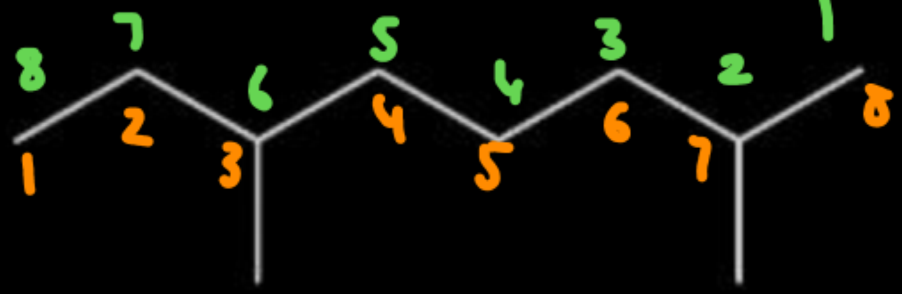
✗ L → 2,5,6 (13)
✓ R → 2,3,6 (11)

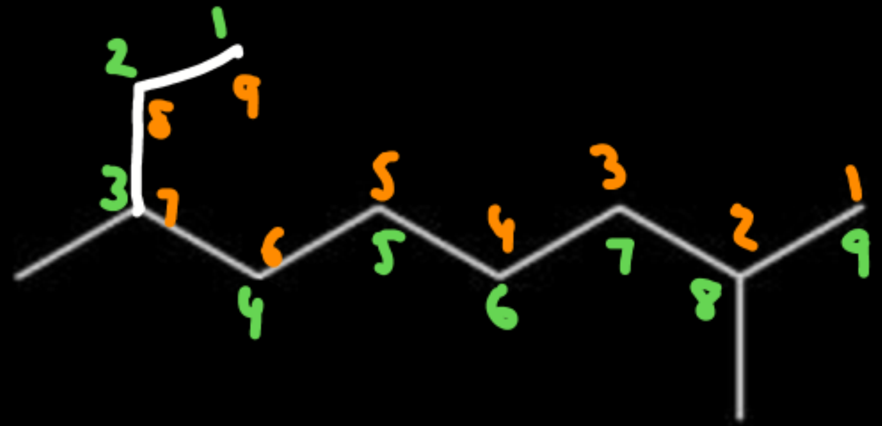




L → 2,4,5,6 ✗ (17)
R → 2,3,4,6 ✓ (15)

✗ L → 3,7 (10)
✓ R → 2,6 (8)

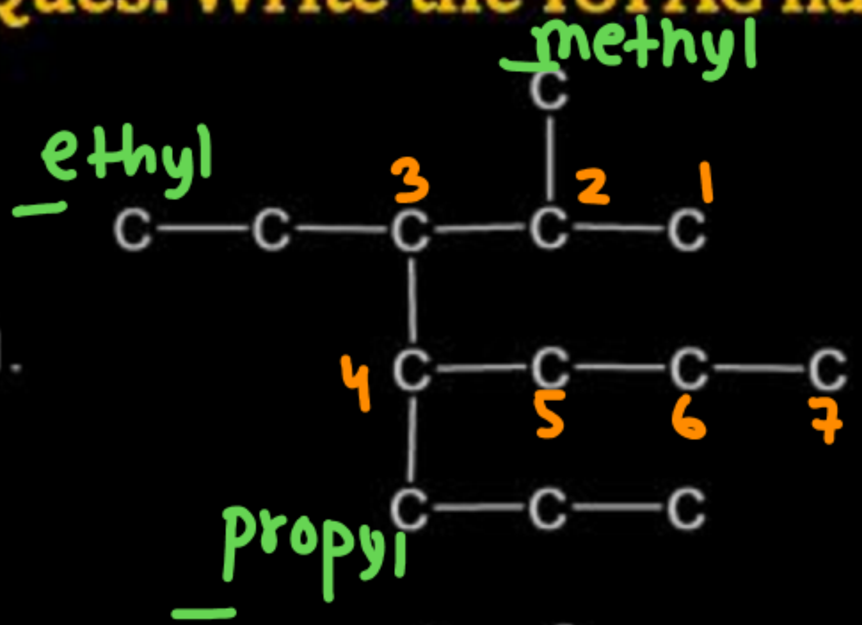




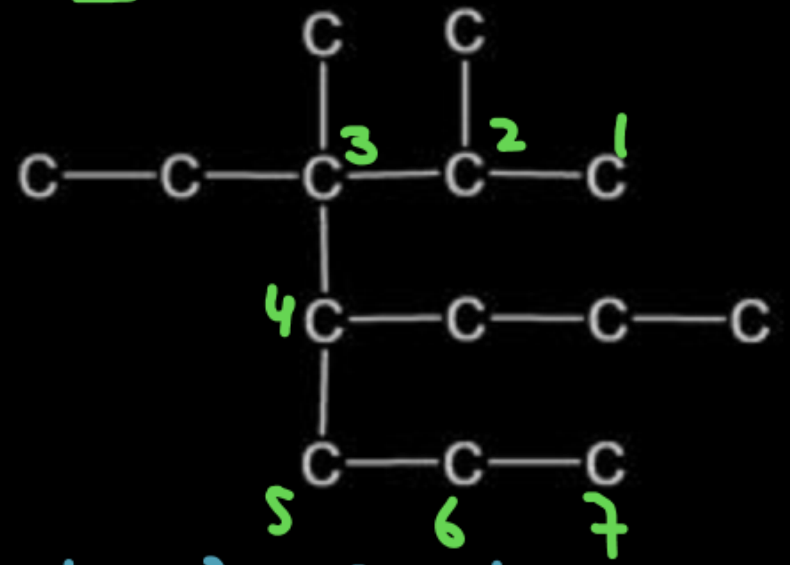
L → 3,8 ✗
R → 2,7 ✓

2,3,4

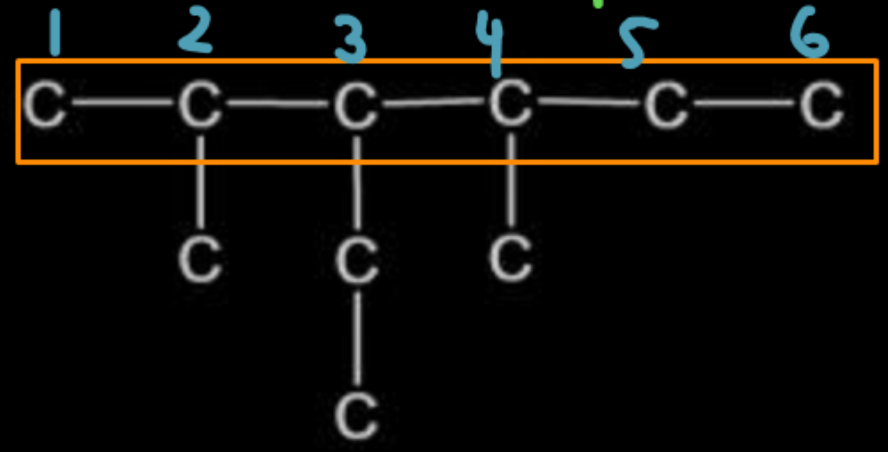
Ques. Write the IUPAC name of following saturated alkane:

1. 

3-ethyl-2-methyl-4-propylheptane

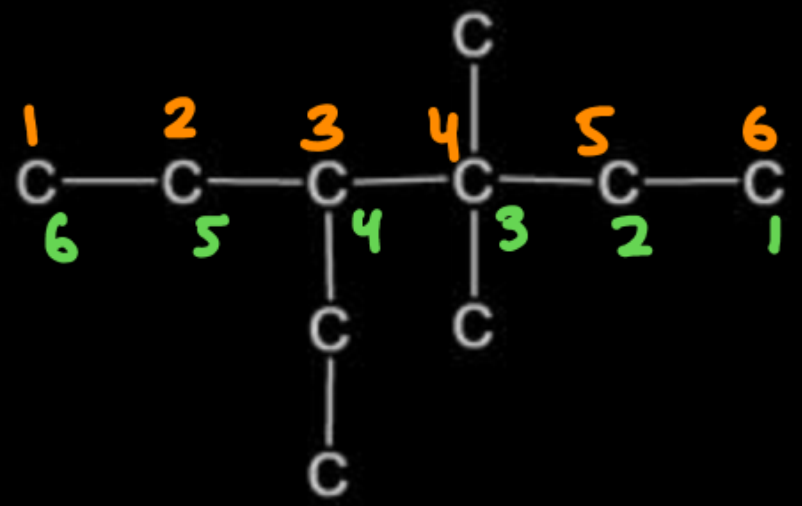
2. 

3-ethyl-2,3-dimethyl-4-propylheptane

3. 

3-ethyl-2,4-dimethyl hexane

4.

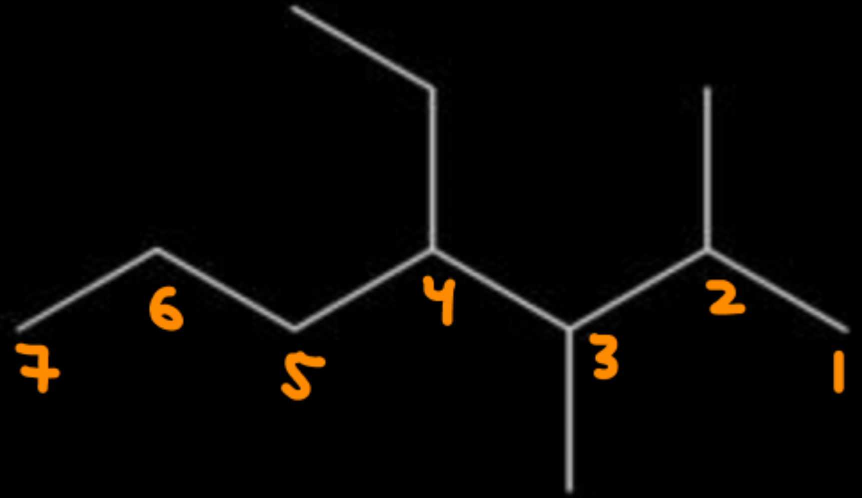


L → 3,4,4 — 11 ✗

R → 3,3,4 — 10 ✓

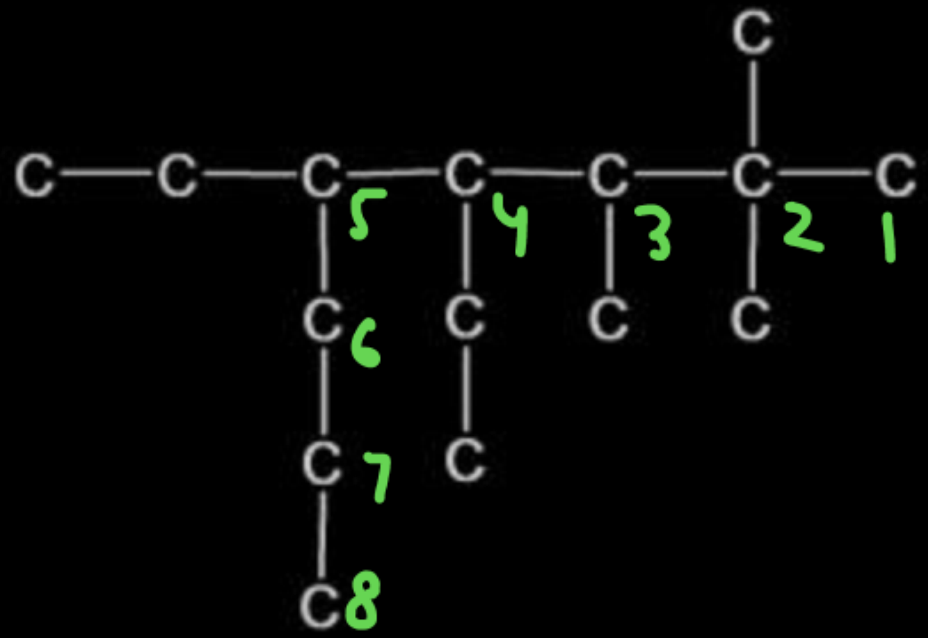
4-ethyl-3,3-dimethylhexane

5.



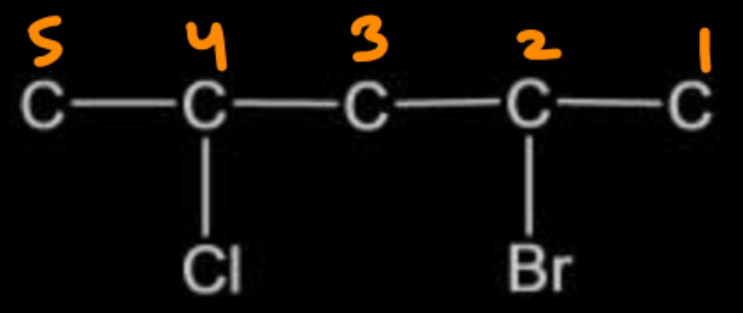
4-ethyl-2,3-dimethylheptane

6.



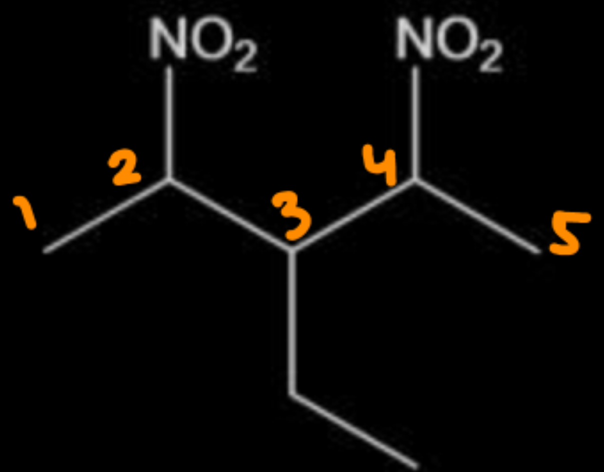
4,5-diethyl-2,2,3-trimethyloctane

7.



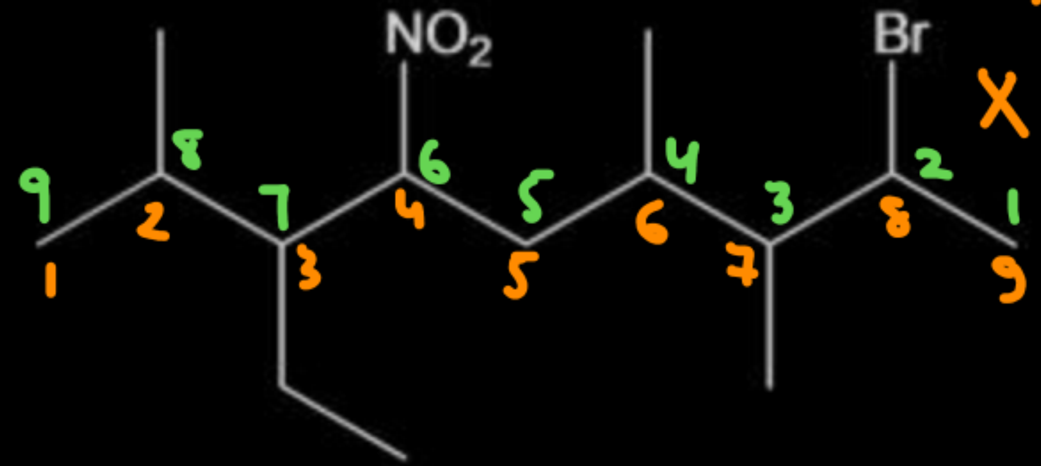
2-Bromo-4-chloropentane

8.



3-ethyl-2,4-dinitropentane

9.



Bromo

✓ R → 2,3,4,6,7,8

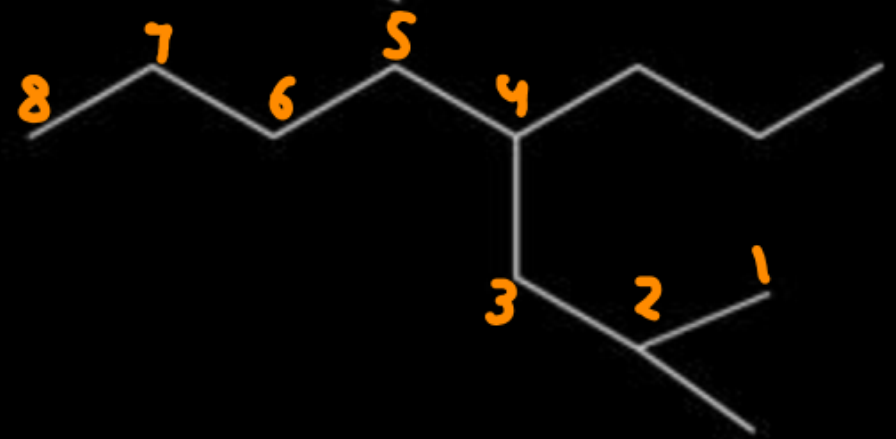
X L → 2,3,4,6,7,8

Methyl

alphabatical Rule

2-Bromo-7-ethyl-3,4,8-trimethyl-6-nitro nonane

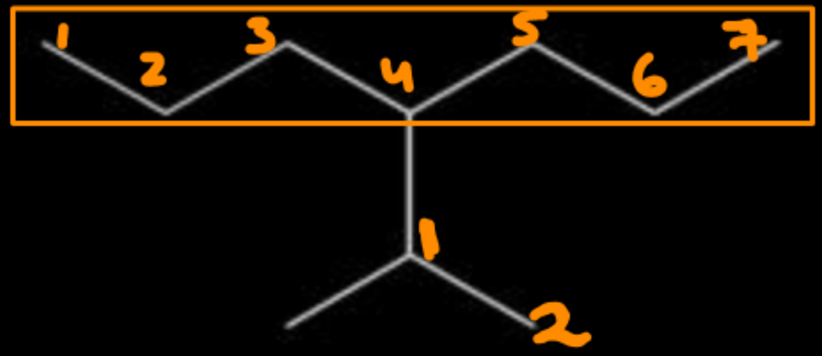
10.



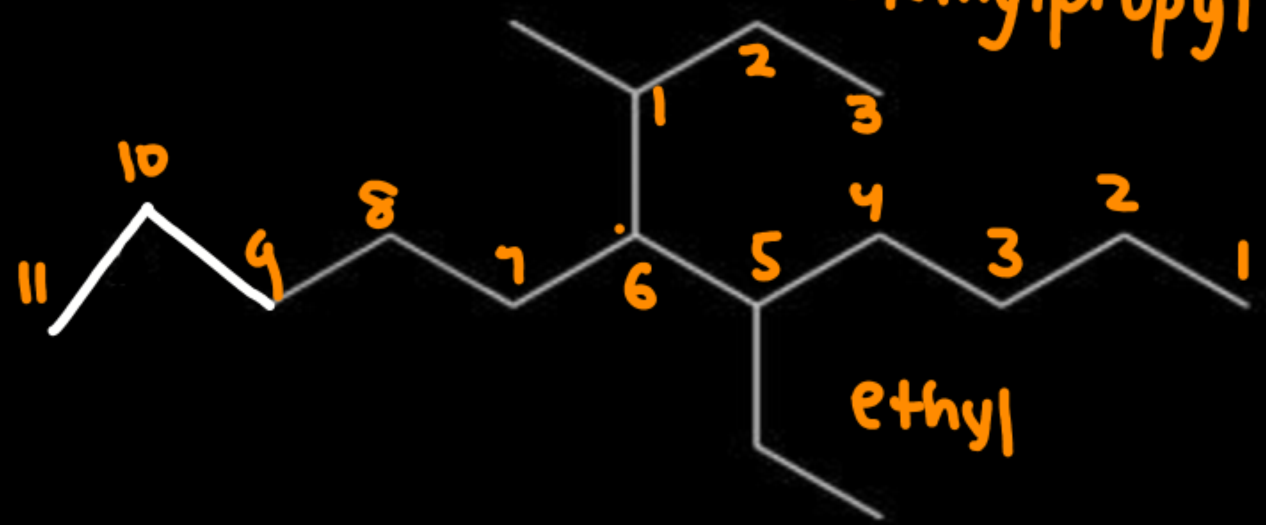
2-methyl-4-propyloctane

Naming of Complex Substituents / Complex Branch

1.

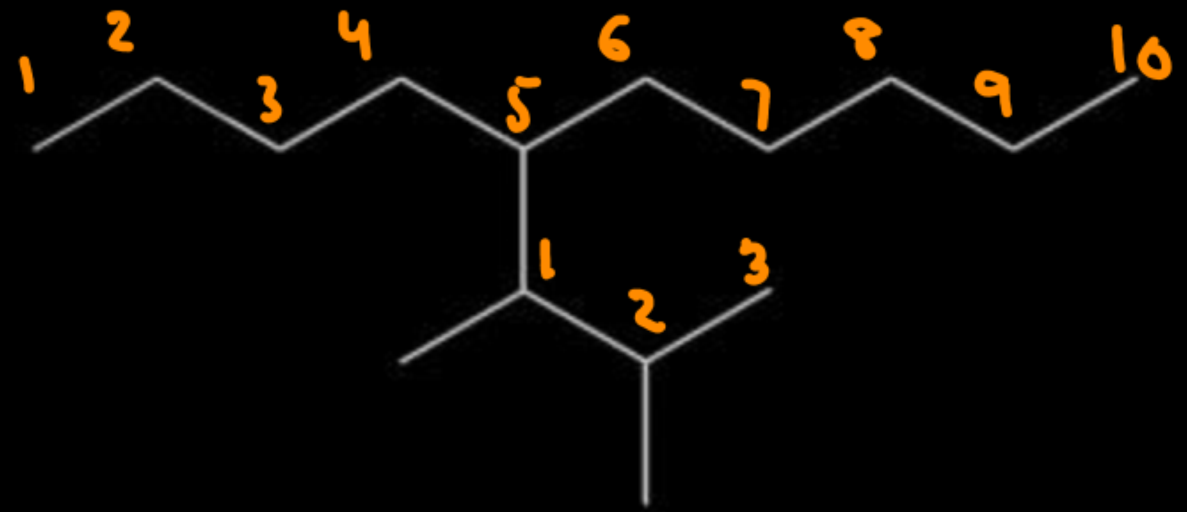


4-(1-methylethyl)heptane / 4-isopropylheptane



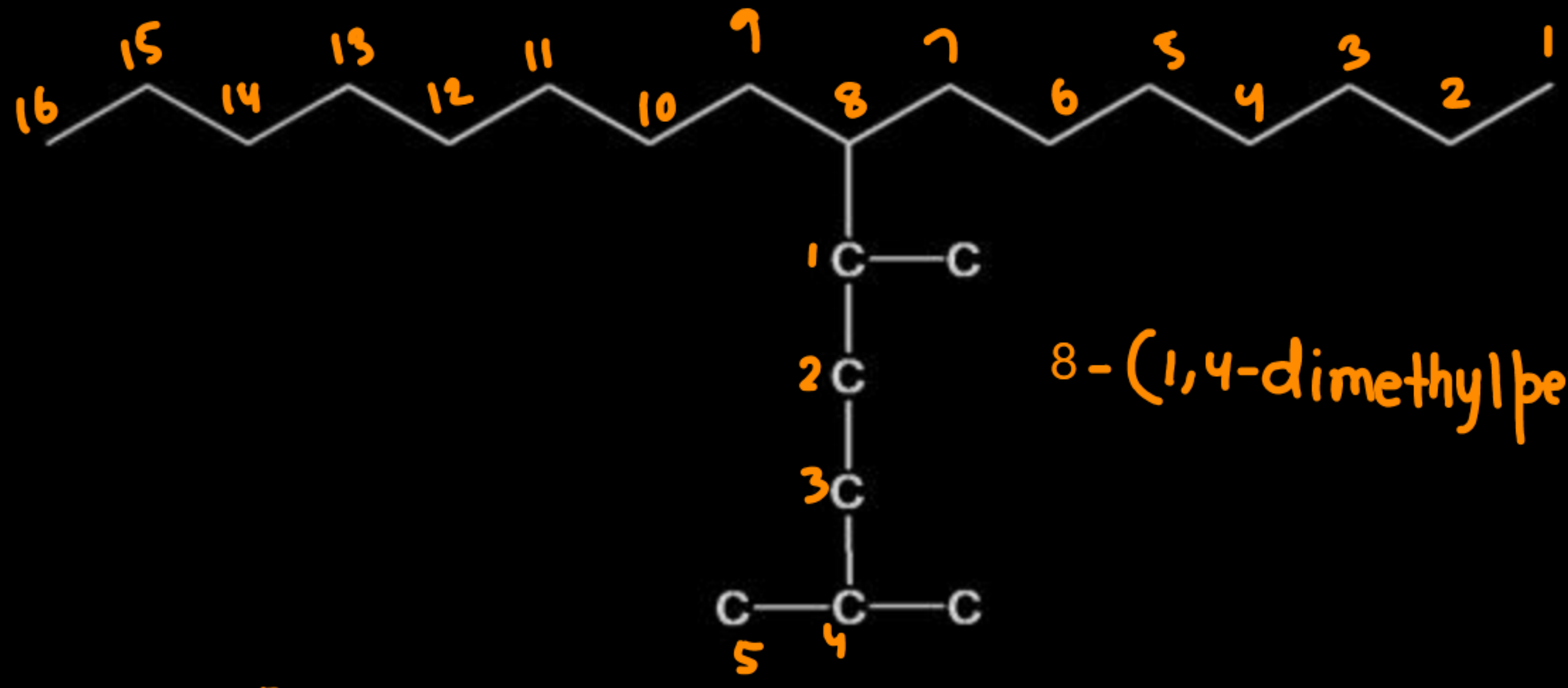
5-ethyl-6-(1-methylpropyl)undecane
or
5-ethyl-6-Secbutylundecane

3.



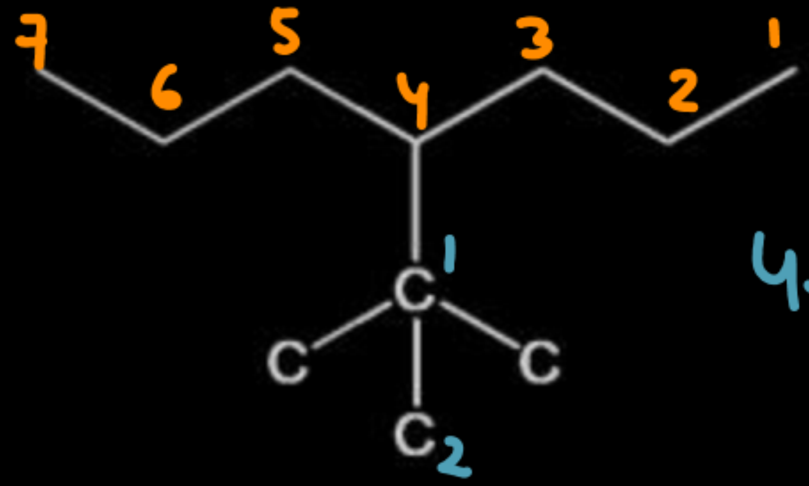
5-(1,2-dimethylpropyl) decane

4.



8-(1,4-dimethylpentyl)hexadecane

5.



4-(1,1-dimethylethyl)heptane

Note: In case of more than one same complex substituents Use:

2 – Bis

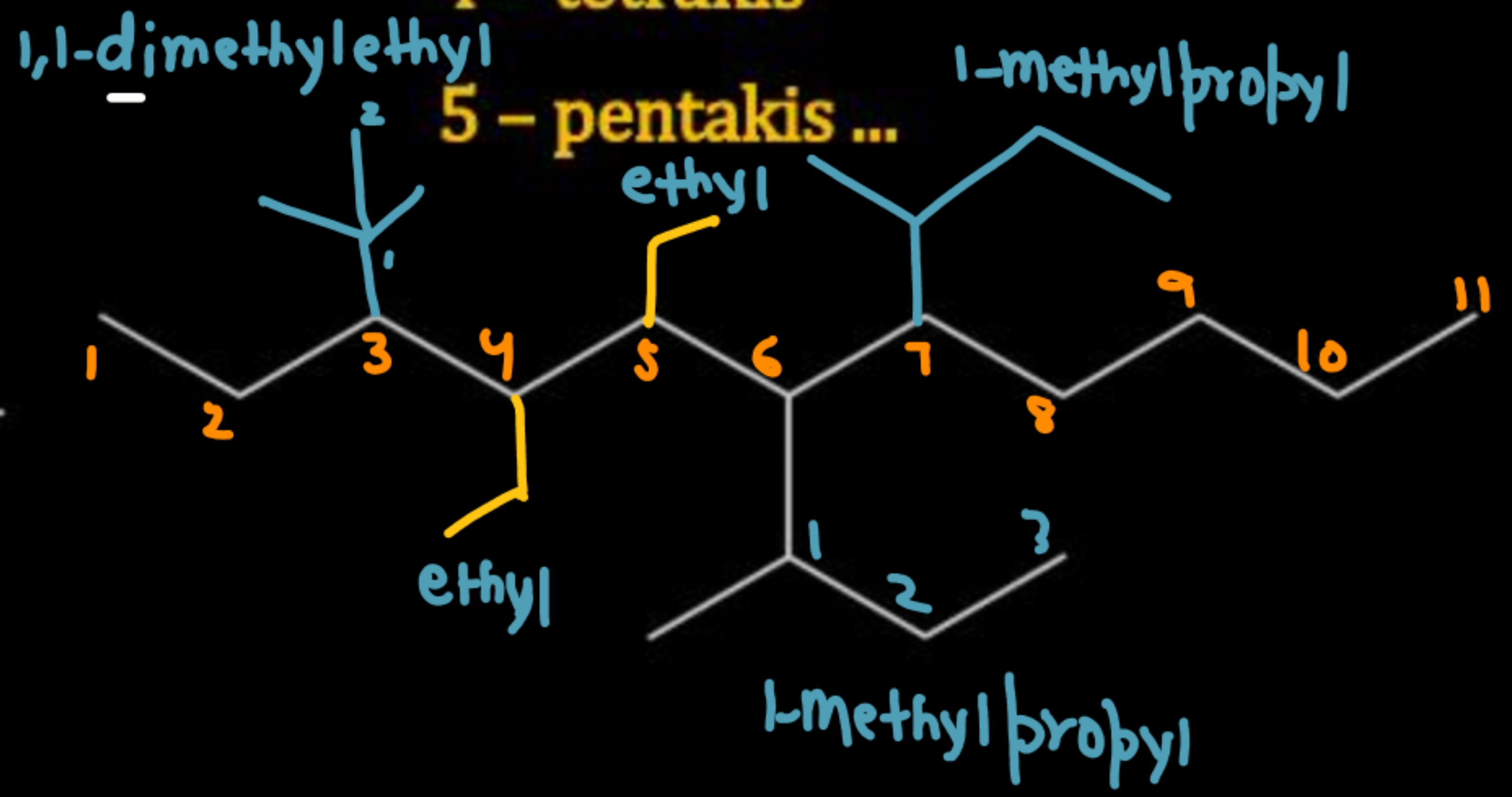
3 – tris

4 – tetrakis

5 – pentakis ...

4,5-diethyl-3-(1,1-dimethylethyl)-6,7-bis(1-methylpropyl) undecane

6.



IUPAC → Saturated OC

Rule 1 (Selection)

max no of Carbon
↓
max no of Carbon & max no of branch

Rule 2 (Numbering)

Lowest Locant Rule
Lowest Locant Sum Rule
Alphabatical Rule

Rule 3 (Naming)

Alphabatical order

(R1) It is that chain which contains max num of multiple bond.

↓

(R2) Unsaturated Pcc → Max Multiple bond & Max num of Carbon

↓

(R3) Max double bond & Max Carbon

↓

(R4) Max double bond & Max Carbon & Max Branch

Rule 2 (Numbering of Pcc) → ① Lowest Locant Rule → Multiple bond should get

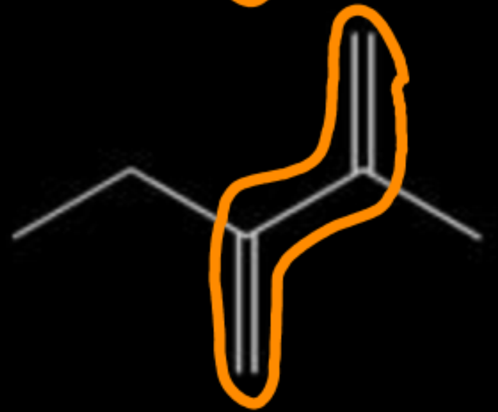
② Lowest Locant sum Rule

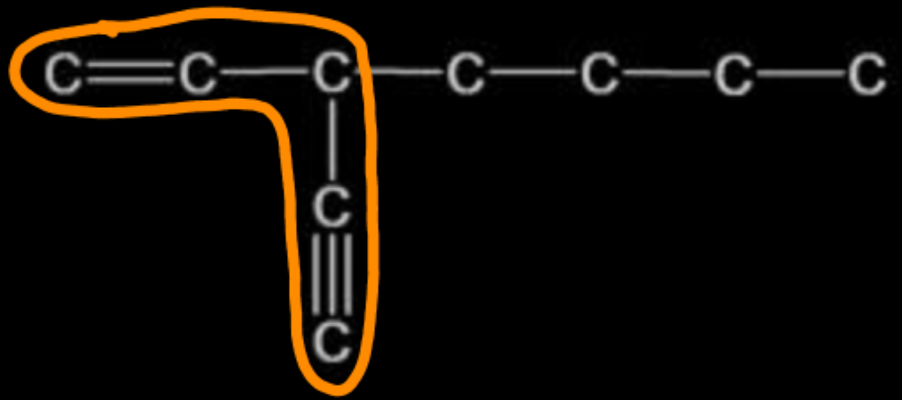
Nomenclature of Unsaturated Hydrocarbon

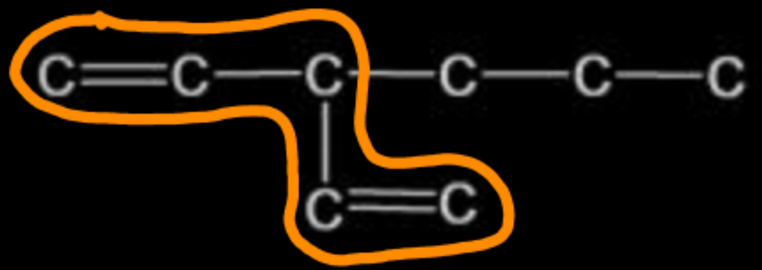
Selection of PCC:

Rule 1: Unsaturated PCC ⟹ Chain having maximum number of multiple bond.

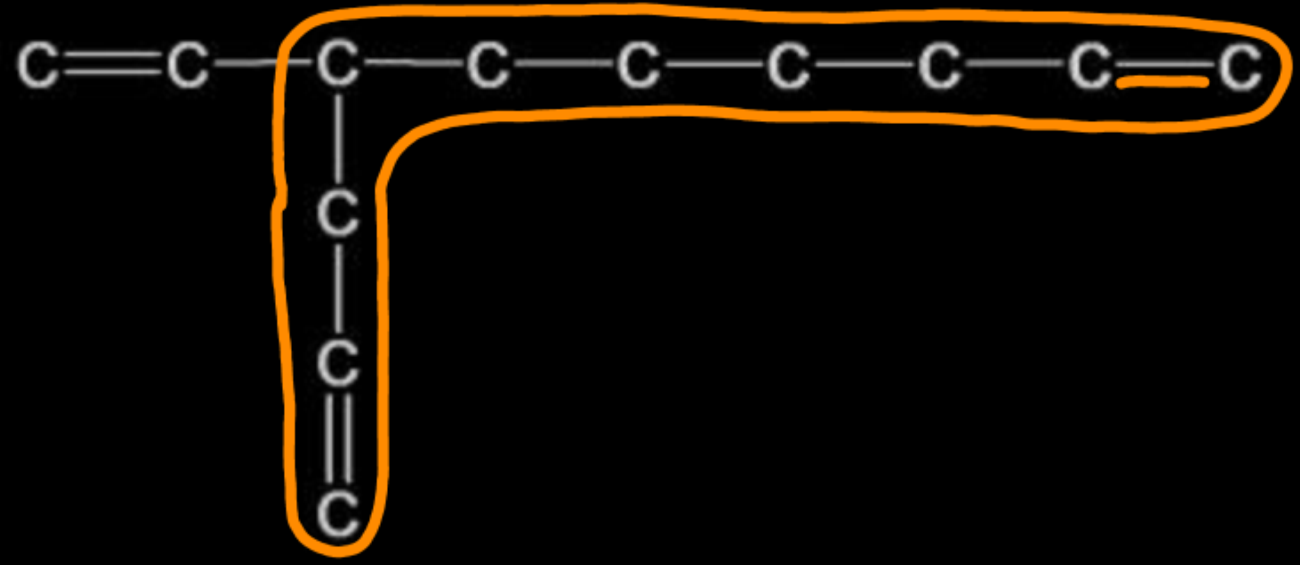
1. 

2. 

3. 

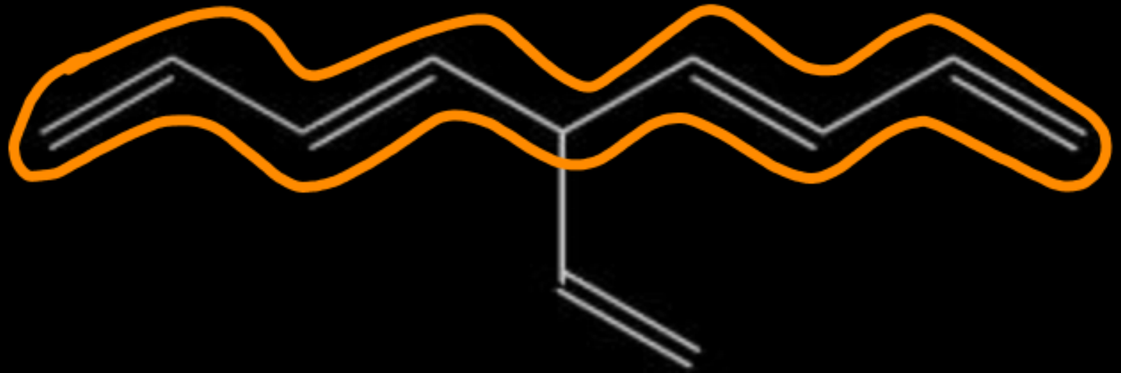
3. 

Rule 2: If number of multiple bond in same in two PCC then select that PCC which has maximum double bond as well as maximum carbon.

4. 

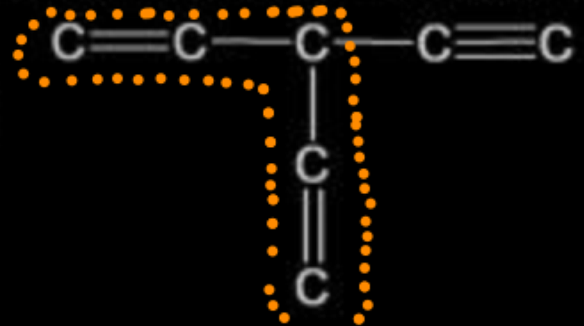
Correct PCC → max multiple bond → max carbon

5. 

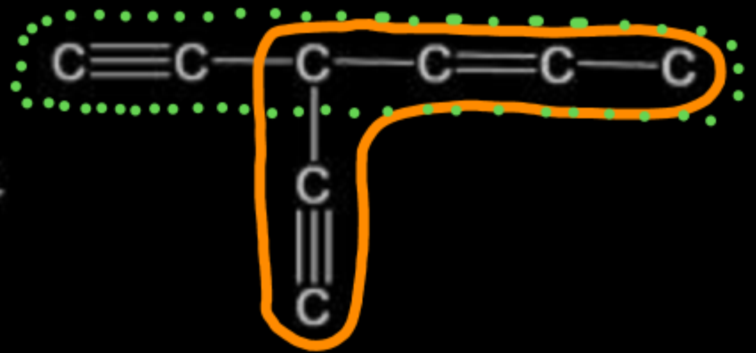
6. 

Rule 3: If number of multiple bond as well as number of carbon is same then select that parent chain which has more number of double bonds than triple bonds.

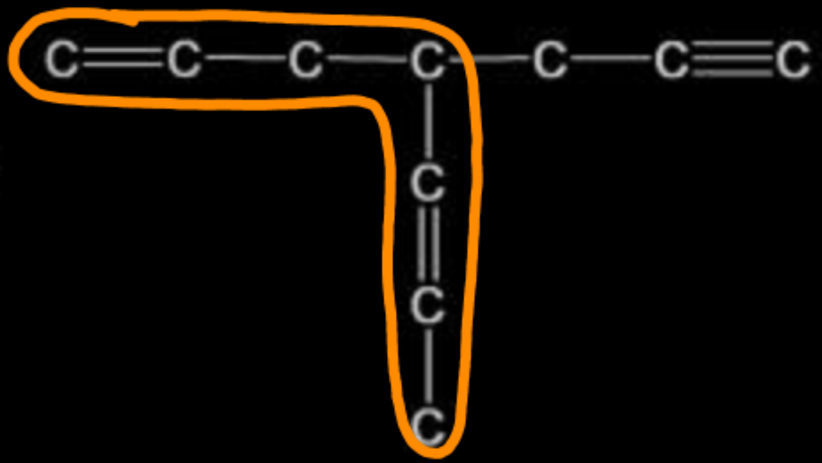
7.



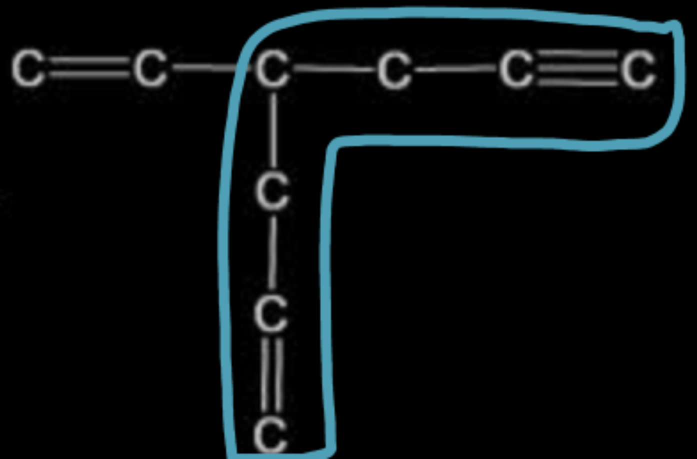
8.



9.

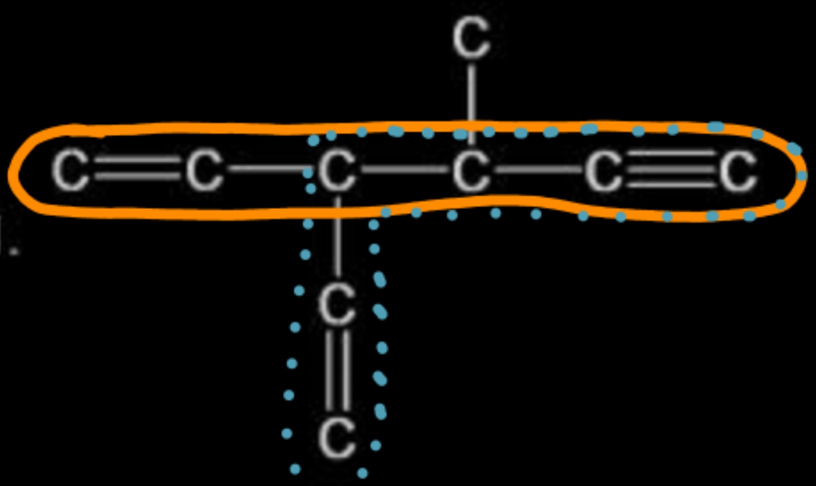


10.

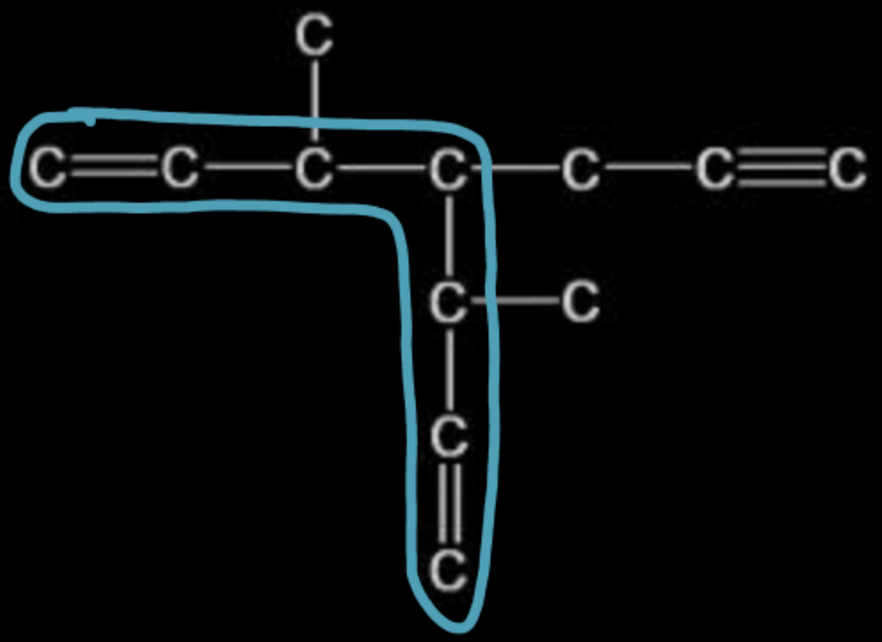


Rule 4: If Rule 1, Rule 2, Rule 3 fails then select that chain which has maximum number of substitutent/branch.

11.



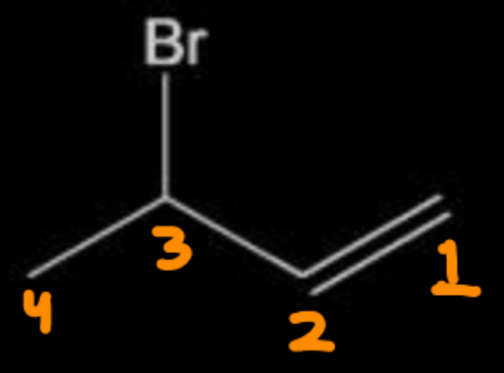
12.



get lowest number.
get priority.

Rule 1 : Numbering is done such that multiple bond gets lowest locant number.

13.

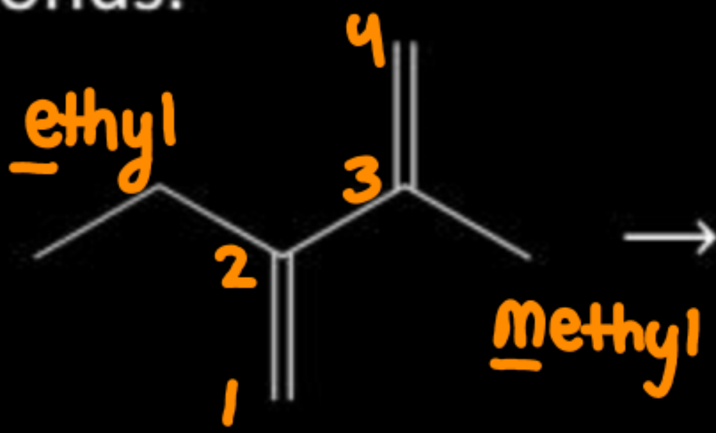


14

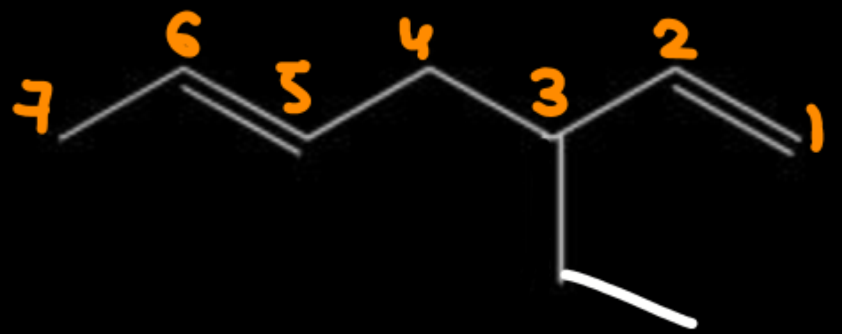


note : Incase of more than one double bond/triple bond always use 'wordroot + a'

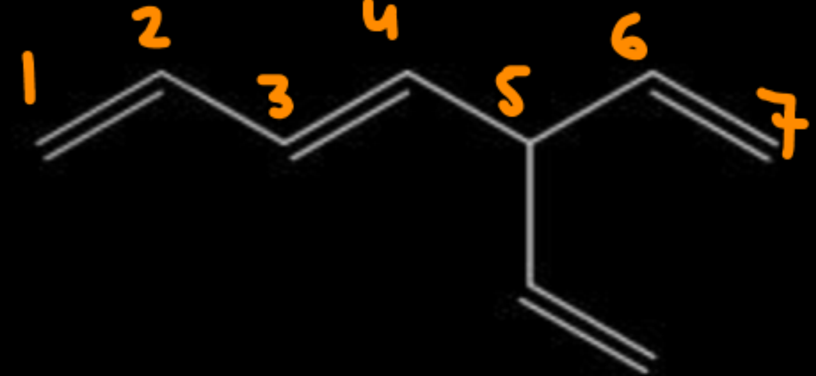
Note: Lowest sum rule & alphabetical order is also applicable here for multiple bonds.

1. 

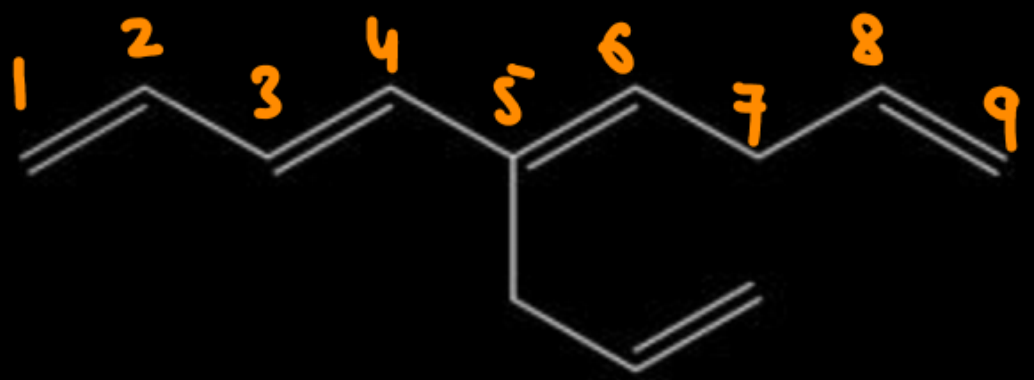
→ 2-ethyl-3-methylbuta-1,3-diene

2. 

→ 3-ethylhepta-1,5-diene

3. 

→ 5-ethenylhepta-1,3,6-triene

4. 

→ 5-propenylnona-1,3,5,8-tetraene

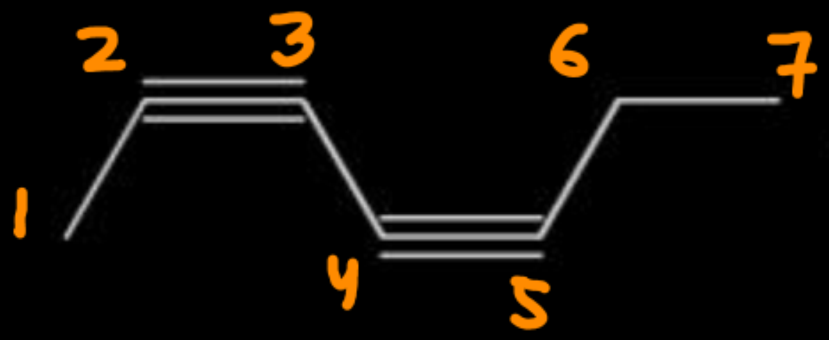
5. 

→ Hex-2-ene-4-yne

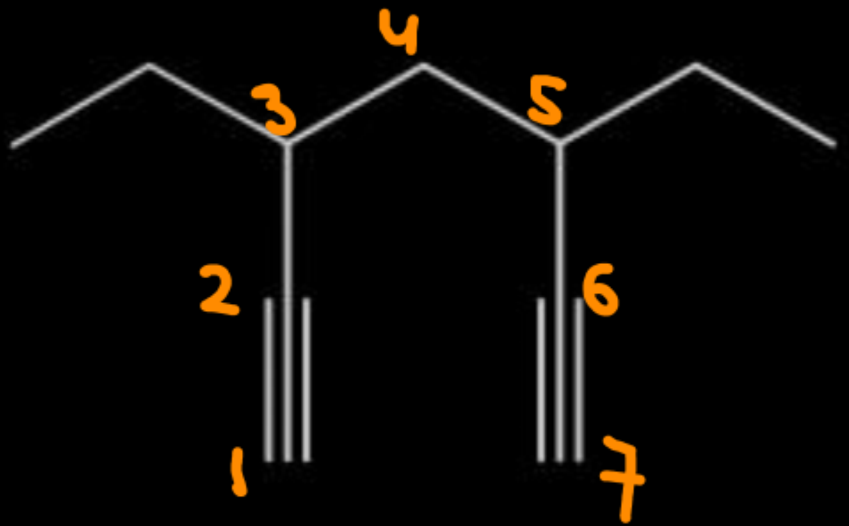
Hex-2-en-4-yne

6. 

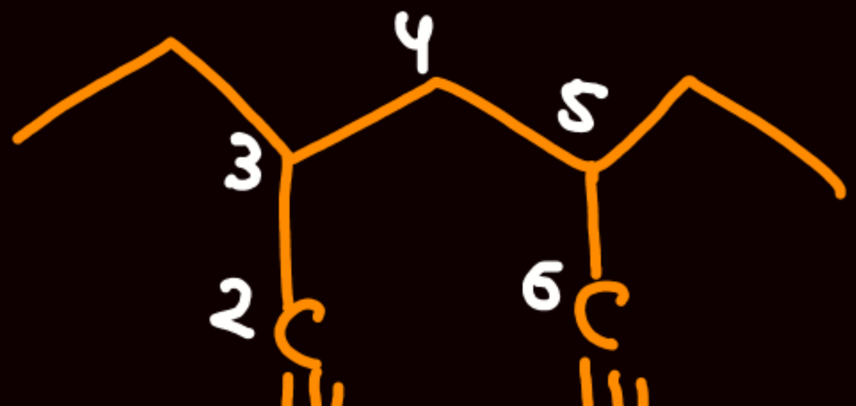
→ Pent-3-ene-1-yne

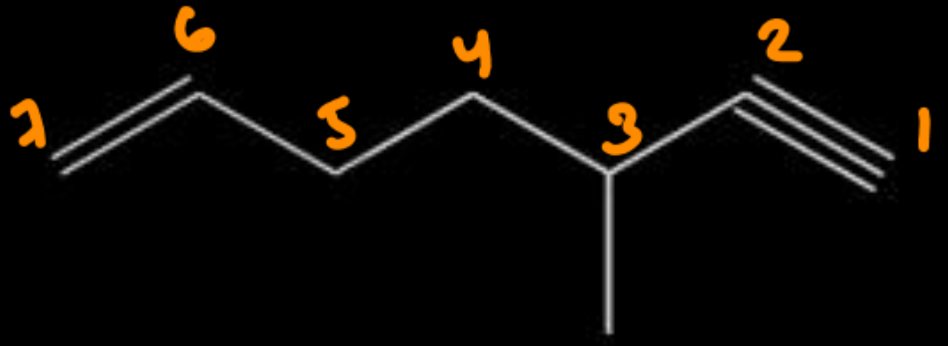
7. 

→ Hepta-2,4-diyne

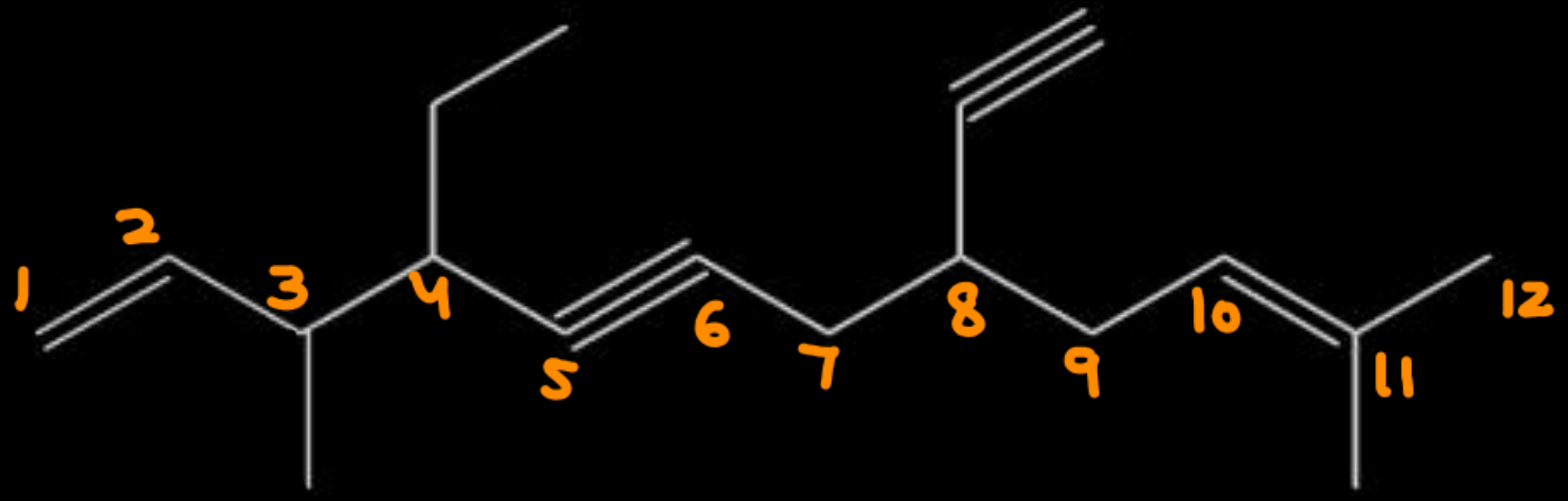
8. 

→ 3,5-diethylhepta-1,6-diyne



9.  → 3-methylhept-6-ene-1-yne

3-methylhept-6-en-1-yne

10.  →

4-ethyl-8-ethynyl-3,11-dimethyldodeca-1,10-diene-5-yne

IUPAC Nomenclature of Cyclic Comp

Rule 1 (selection of Pcc) → (R1) In case of cyclic Comp → Pcc is that chain which has max num of Carbon.

↓

(R2) If num of Carbon in Ring & open chain is same then Pcc is Ring (Ring is given priority)

↓

(R3) If num of Carbon in Ring & open chain is same & open chain has more number of branch then our Pcc is open chain.
if Ring has more num of branch then our Pcc is Ring.
if both has same branch then Ring is our priority.

↓

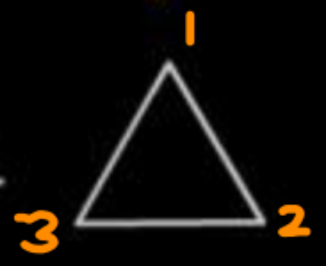
In case of multiple bond → Pcc is that chain which has Max num of multiple bond.

↓

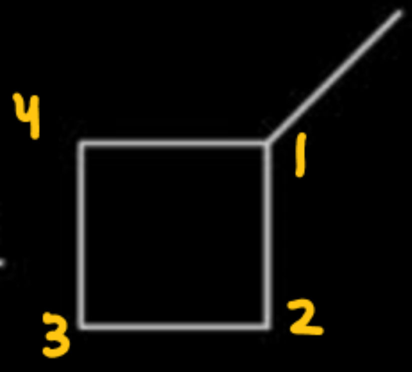
(double & triple bond)

Nomenclature of Cyclic Compounds

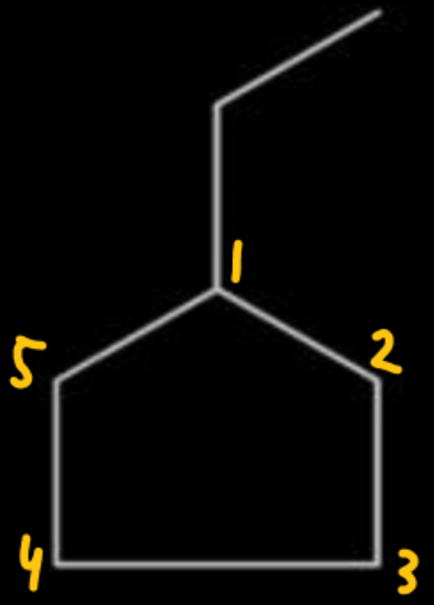
Examples:

1. 

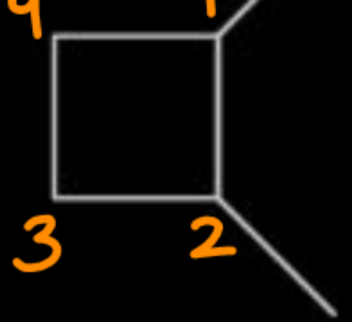
→ cyclopropane

2. 

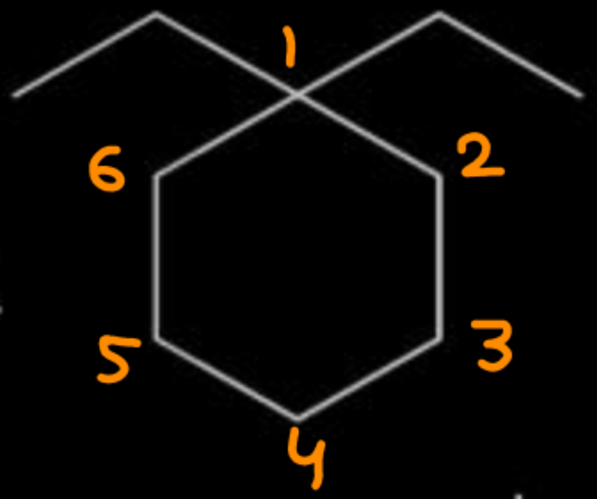
→ 1-methylcyclobutane

3. 

→ 1-ethylcyclopentane

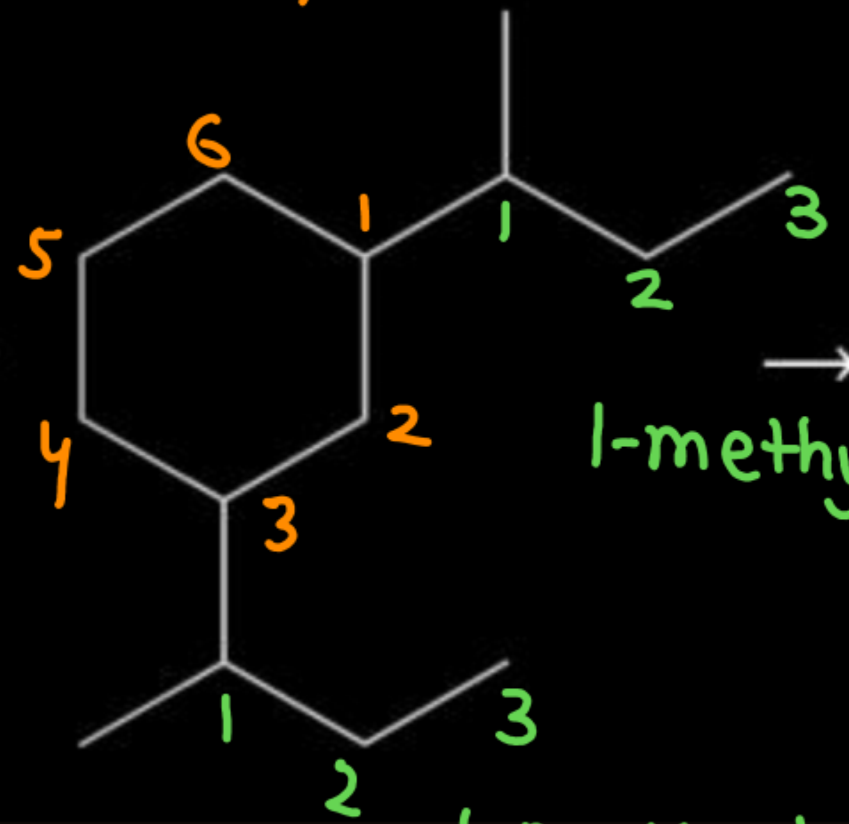
4. 

→ 1,2-dimethylcyclobutane

5. 

~~21012~~

→ 1,1-diethylcyclohexane

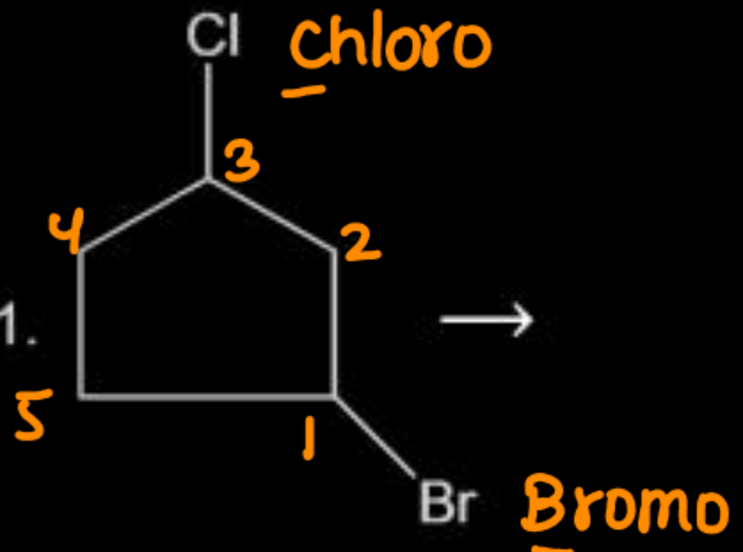
6. 

→ 1-methylpropyl

1-methylpropyl

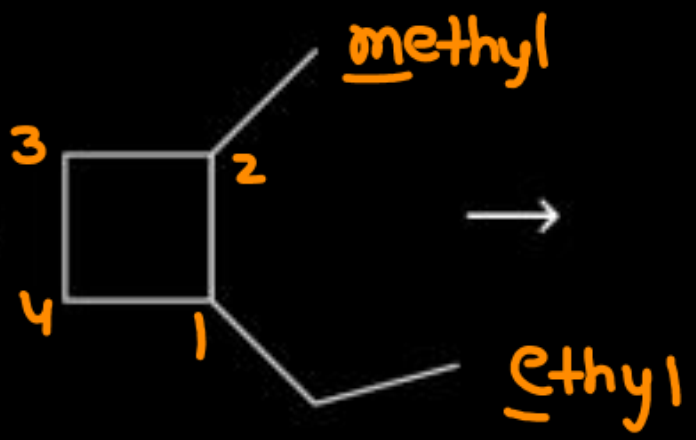
1,3-bis(1-methylpropyl)cyclohexane

1,3-disecbutylcyclohexane

1. 

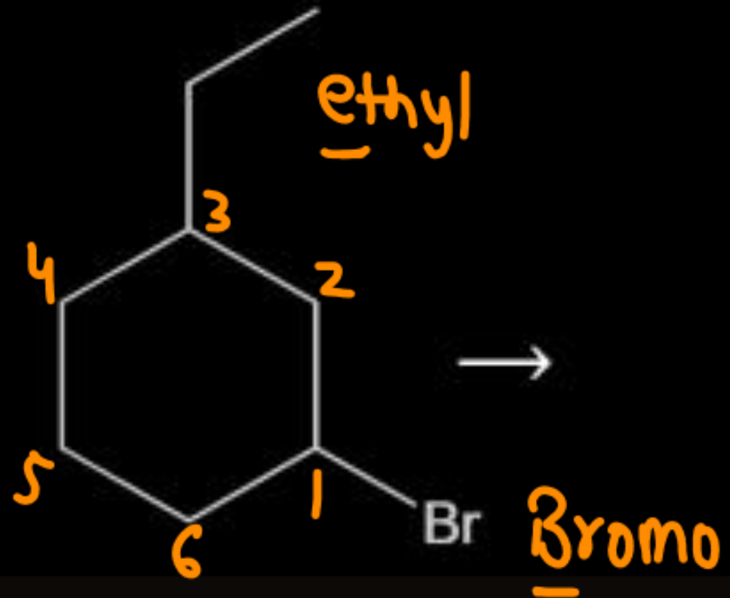
→ ~~2x10x2~~

1-Bromo-3-chlorocyclopentane

2. 

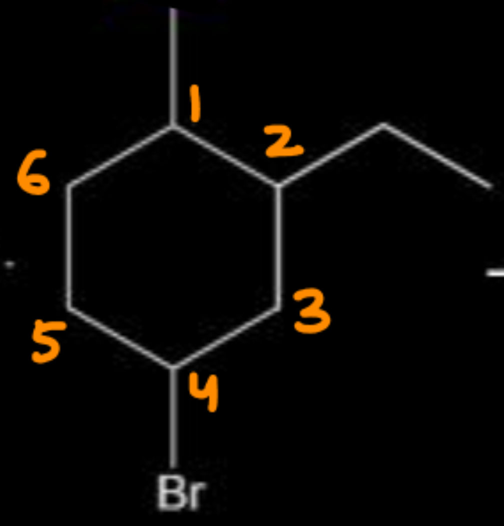
→ ~~2x10x2~~

1-ethyl-2-methylcyclobutane

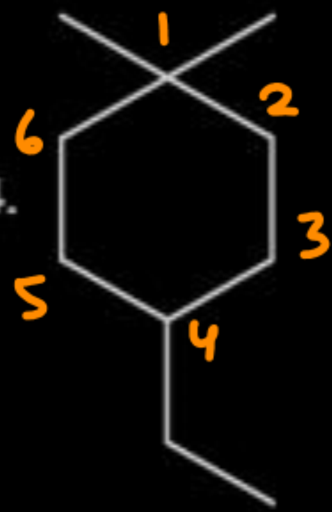
3. 

→ ~~2x10x2~~

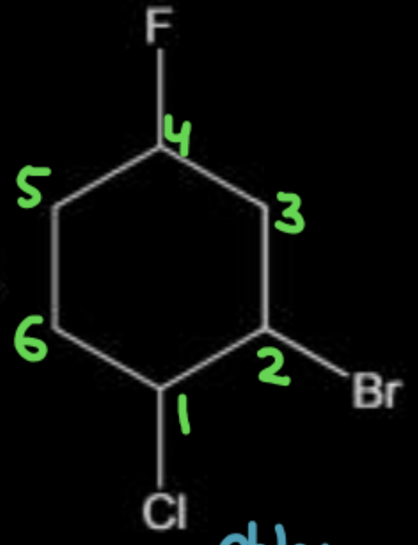
1-Bromo-3-ethylcyclohexane

1. 

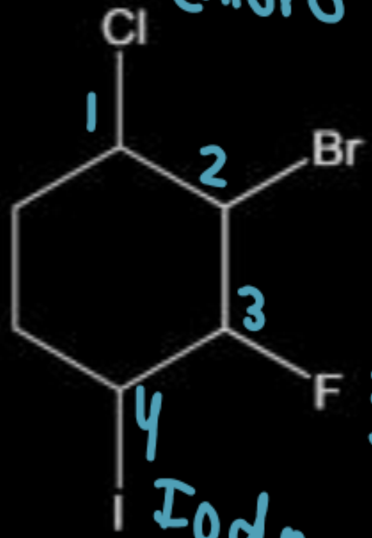
→ 4-Bromo-2-ethyl-1-methyl cyclohexane

4. 

1,1,4 → 4-ethyl-1,1-dimethyl cyclohexane

2. 

→ 2-Bromo-1-chloro-4-fluorocyclohexane

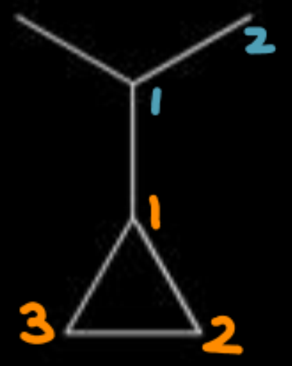
3. 

chloro Bromo Fluoro Iodo

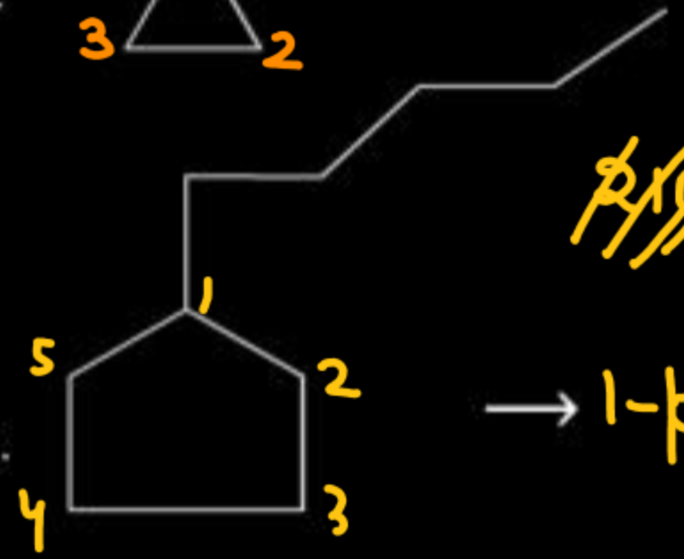
→ 2-Bromo-1-chloro-3-fluro-4-Iodocyclohexane

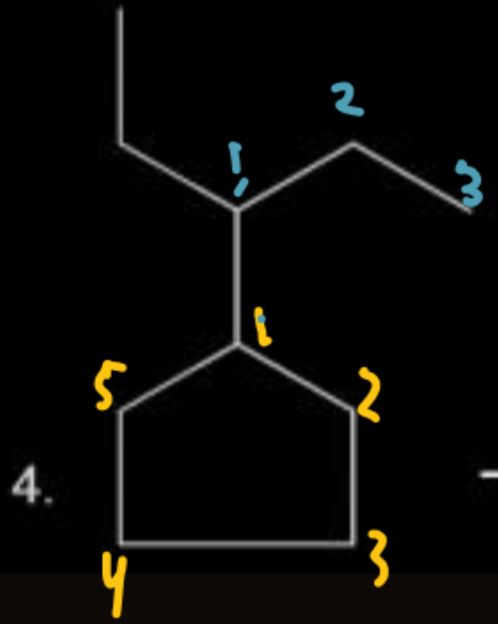
1.  → 1-propylcyclopropane

21012

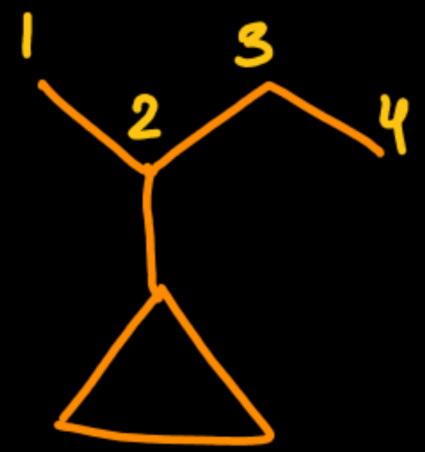
2.  → 1-isopropylcyclopropane

1-(1-methylethyl)cyclopropane

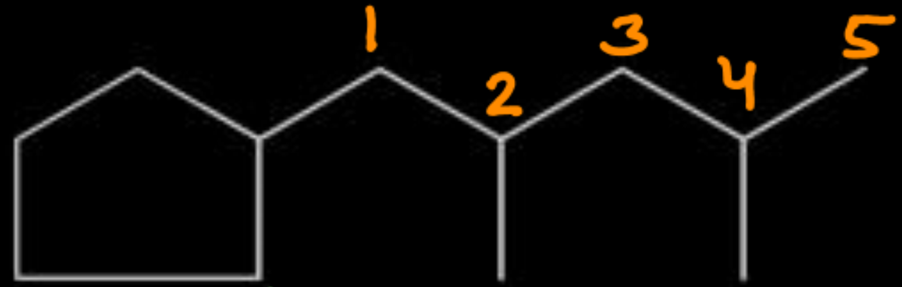
3.  → 1-pentylcyclopentane

4.  →

1-(1-ethylpropyl)cyclopentane

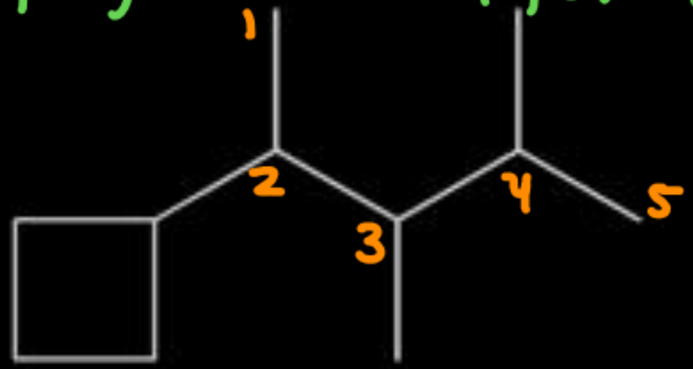


2-cyclopropylbutane

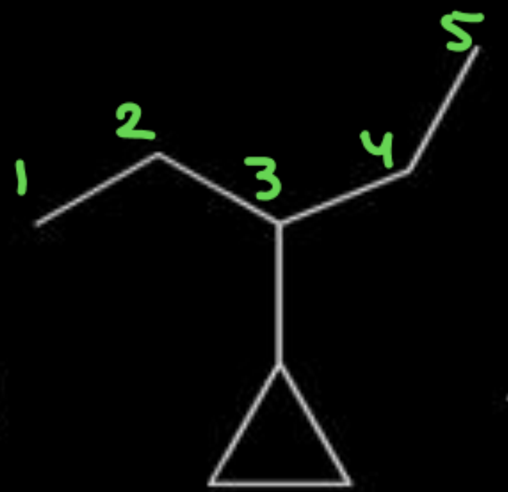
5. 

→ 1-cyclopentyl-2,4-dimethylpentane

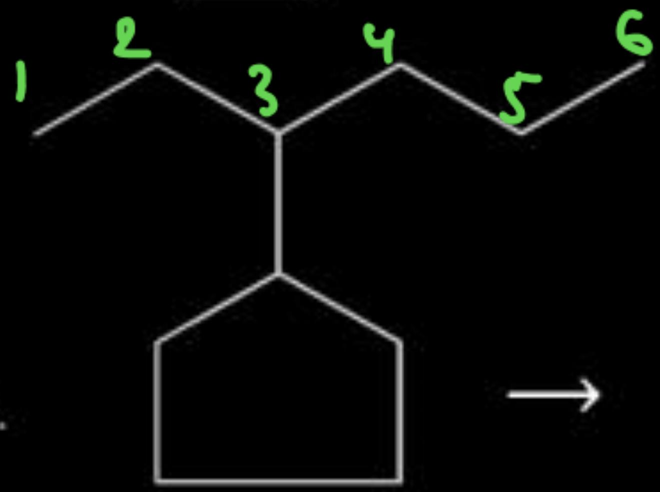
Note → If cyclo is used for branch then cyclo is considered in alphabatical order.

6. 

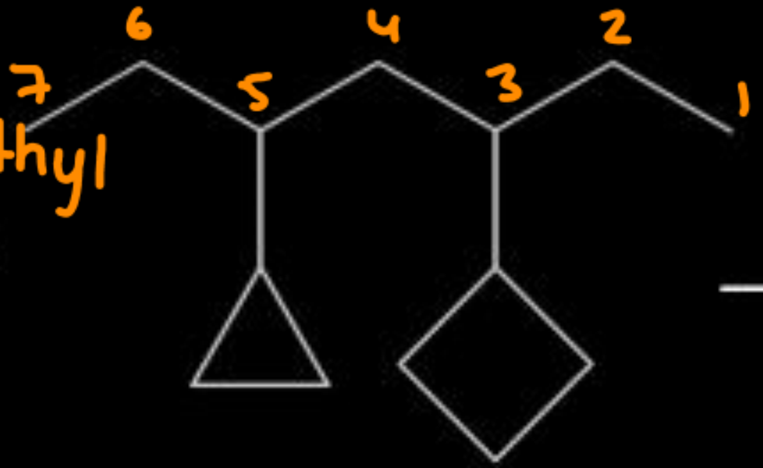
→ 2-cyclobutyl-3,4-dimethyl pentane

7. 

→ 3-cyclopropylpentane

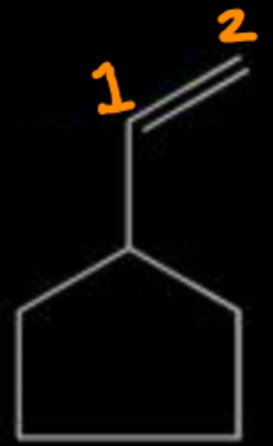
8. 

→ 3-cyclopentylhexane

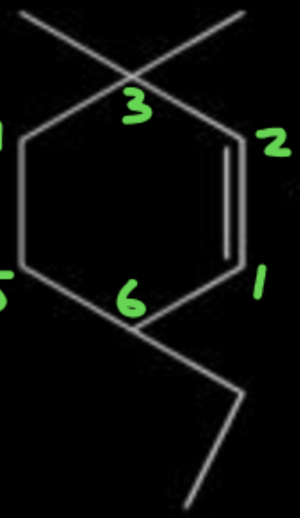
9. 

→ 3-cyclobutyl-5-cyclopropylheptane

Priority →
① multiple bond
② Branch

1. 

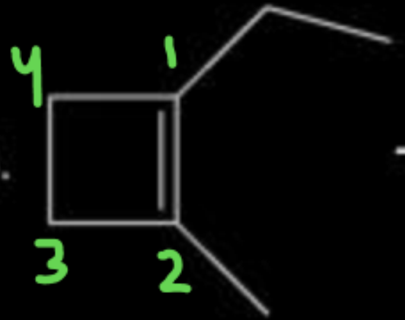
→ 1-cyclopentyleth-1-ene

2. 

→ ~~1,3,6,6~~

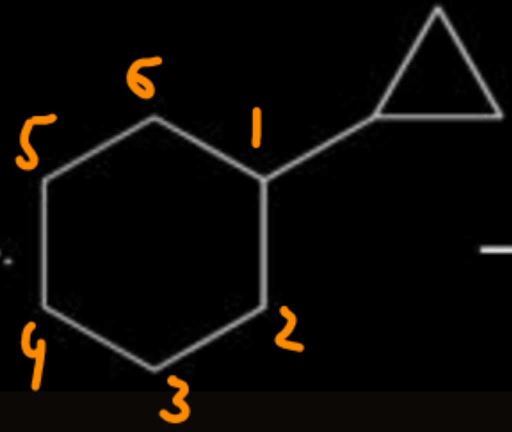
1,3,3,6 ✓

6-ethyl-3,3-dimethylcyclohex-1-ene

3. 

→ 1-ethyl-2-methylcyclobutene

1-ethyl-2-methylcyclobut-1-ene

4. 

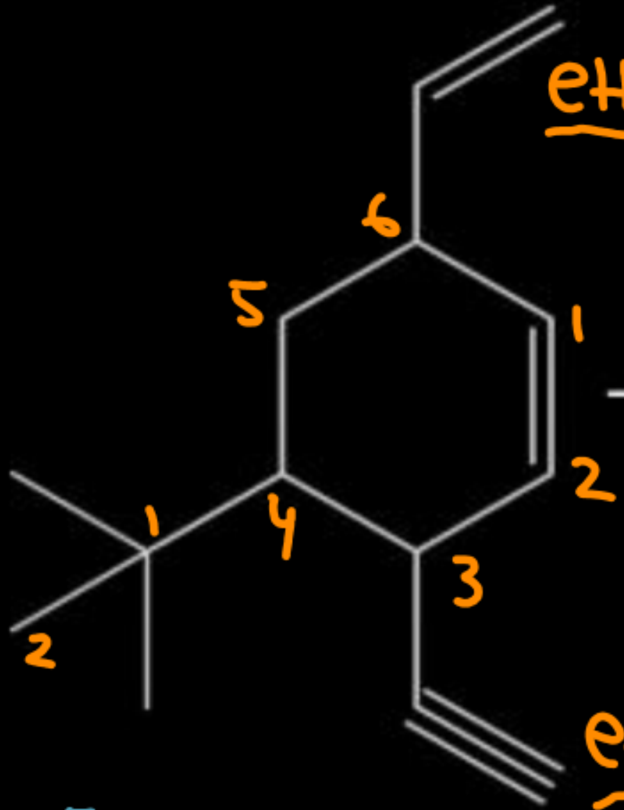
→ 1-Cyclopropylcyclohexane

5. 

→ 3-cyclobutyl prop-1-en

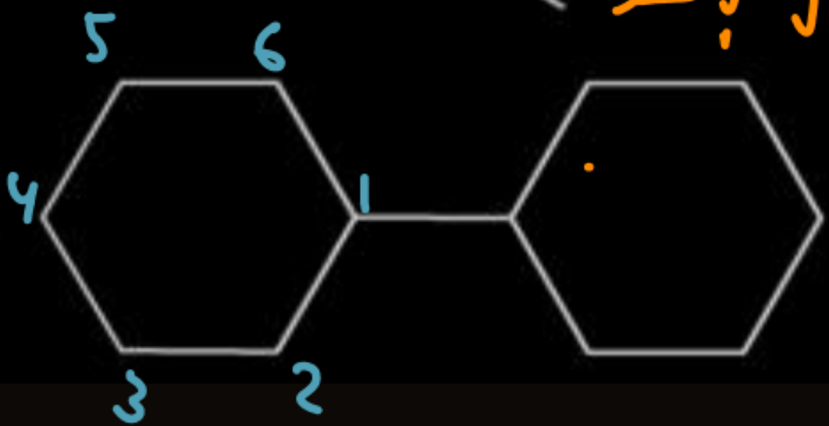
6) 

→ 1-cyclobutylbuta-1,3-diene

7. 

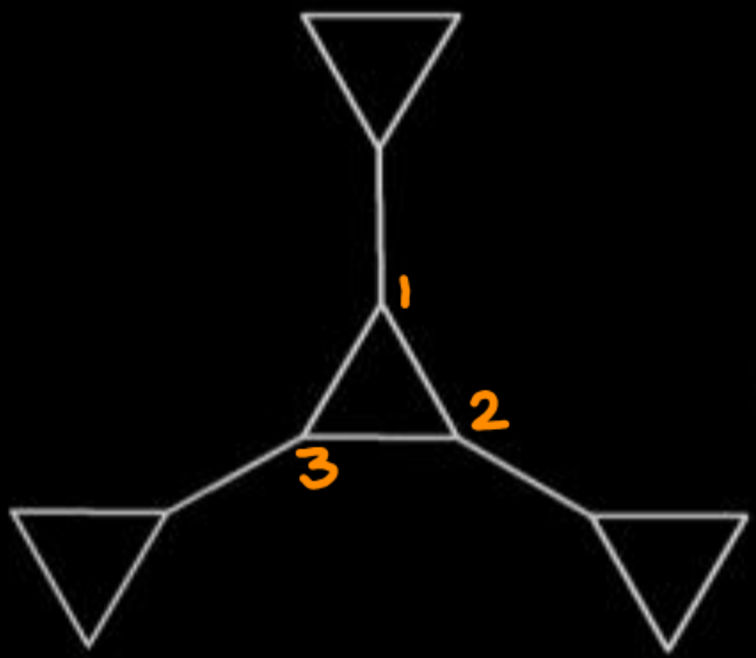
→ 6-ethenyl-3-ethynyl-4-tertbutyl cyclohex-1ene

6-ethenyl-3-ethynyl-4-(1,1-dimethylethyl) cyclohex-1-en

8. 

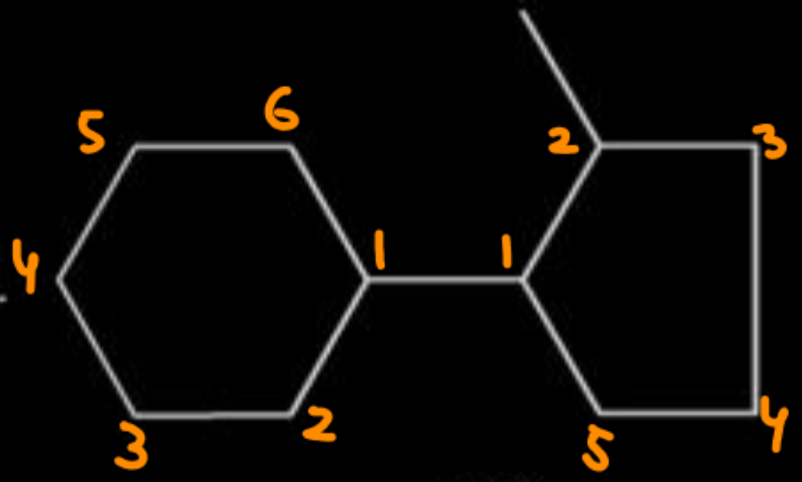
→ 1-cyclohexyl cyclohexane

9.



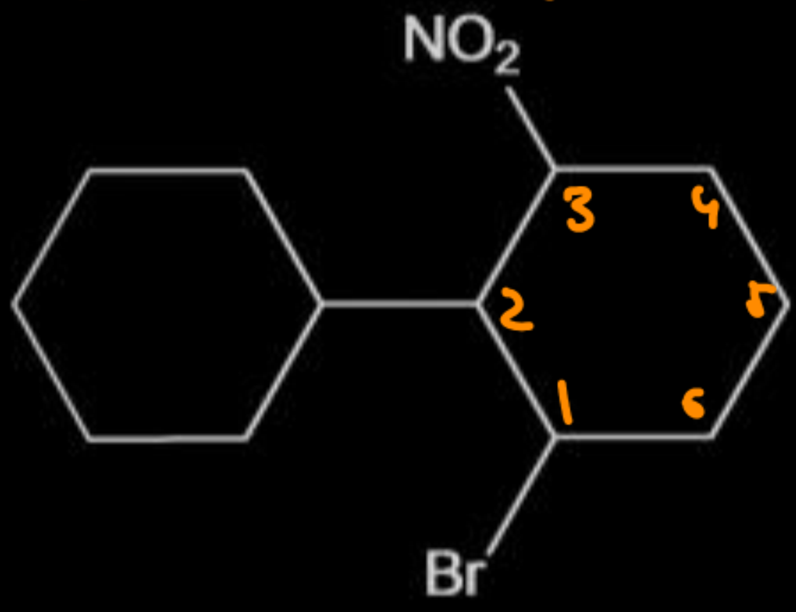
→ 1,2,3-tricyclopropylcyclopropane

10.



→ 1-(2-methylcyclopentyl) cyclohexane

11.



→ 1-Bromo-2-cyclohexyl-3-nitrocyclohexane

IUPAC Nomenclature of monofunctional Group

Seniority Table / Priority Table

	Prefix		2' suffix
① Carboxylic acid $-COOH$ $-C(=O)-O-H$	Carboxy	$-\overset{*}{C}(=O)-OH$	oic acid
		$-C(=O)-OH$	Carboxylic acid
② Sulphonic acid $-SO_3H$ $-S(=O)_2-O-H$	Sulpho	$-S(=O)_2-OH$	Sulphonic acid
③ Acid Anhydride $-COOOC-$ $-CO_3C-$ $-C(=O)-O-C(=O)-$	X	$-C(=O)-O-C(=O)-$	oic anhydride

Functional group	Prefix	2° suffix
④ Ester $-COOR$ $-C(=O)-O-R$	① Alkoxy Carbonyl ② Alkanoyl oxy	$-C^{*}(=O)-O-R$ Alkyl ...... oate $-C(=O)-O-R$ Alkyl Carboxylate
⑤ Acid Halide $-COX$ $-C(=O)-X$	Haloformyl	$-C^{*}(=O)-X$ oyl halide $-C(=O)-X$ Carbonyl halide
⑥ Amide $-CONH_2$ $-C(=O)-NH_2$	Carbamoyl	$-C^{*}(=O)-NH_2$ amide $-C(=O)-NH_2$ Carbamide Carboxamide *
⑦ cyanide $-CN$ $-C\equiv N$	cyano	$-C^{*}\equiv N$ nitrile $-C\equiv N$ Carbonitrile
⑧ Isocyanide $-NC$ $-\overset{\oplus}{N}\equiv C$	Isocyano	$-N\equiv C$ Isonitrile

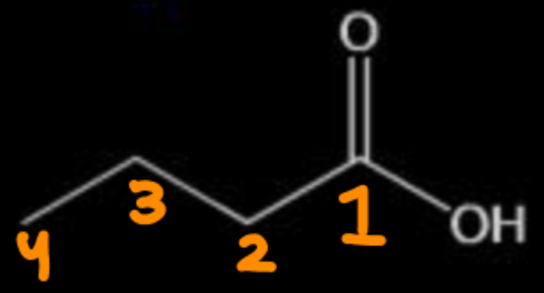
9	aldehyde $-CHO$ $-C(=O)-H$	oxo/formyl	$-C(=O)-H$	al
			$-C(=O)-H$ *	Carbaldehyde
10	Ketone $-CO-$ $-C(=O)-$	keto/oxo	$-C(=O)-$	one
11	Alcohol $-OH$ $-O-H$	Hydroxy	$-OH$	ol
12	Thioalcohol $-SH$ $-S-H$	mercepto	$-SH$	thiol
13	Amine $-NH_2$	amino	$-NH_2$	amine

PRIORITY RULE → Functional Grp > Multiple bond > Num of Carbon > Branc

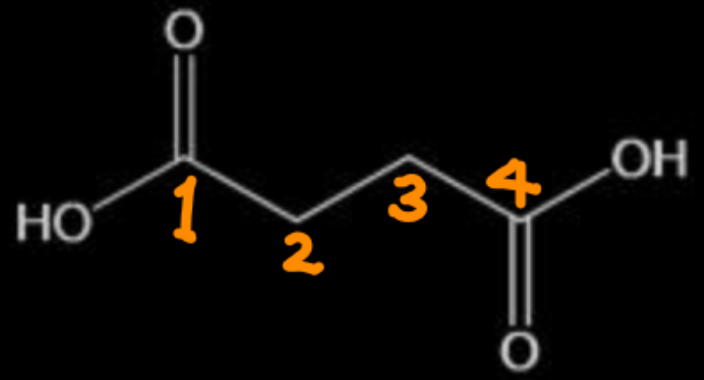
Naming of Monofunctional Group

Carboxylic Acid

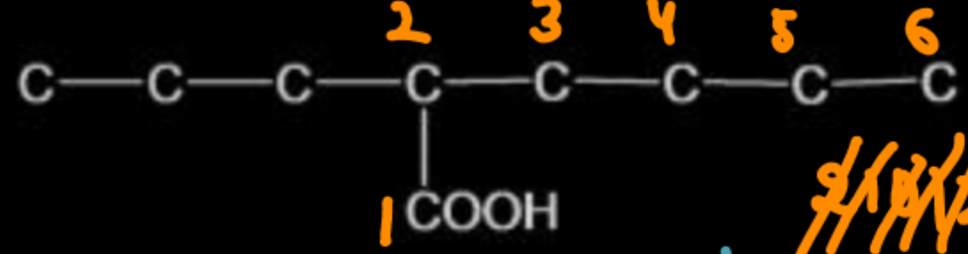
Examples:

1. 

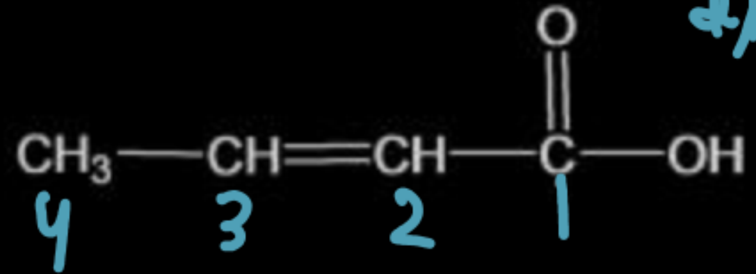
→ Butane-1-oicacid   Butan-1-oicacid   Butanoicacid

2. 

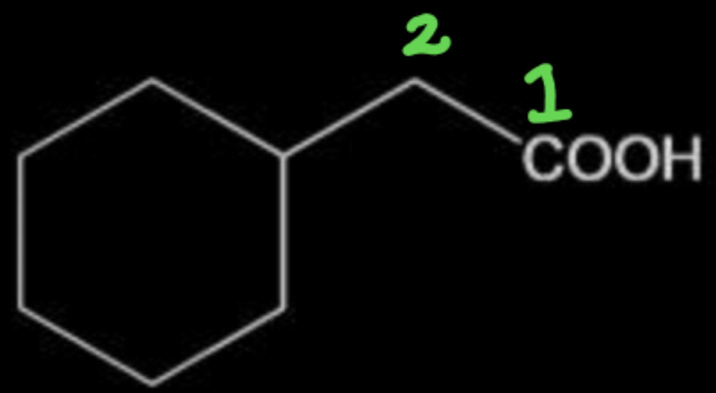
→ Butane-1,4-dioicacid

3. 

→ 2-propylhexane-1-oicacid

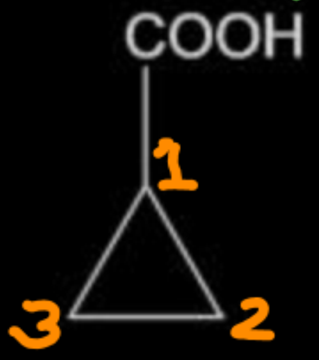
4. 

→ But-2-ene-1-oicacid

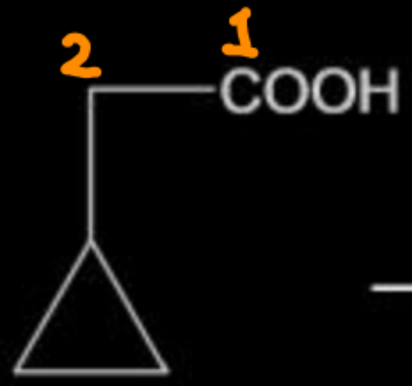
5. 

→ 2-cyclohexylethane-1-oic acid

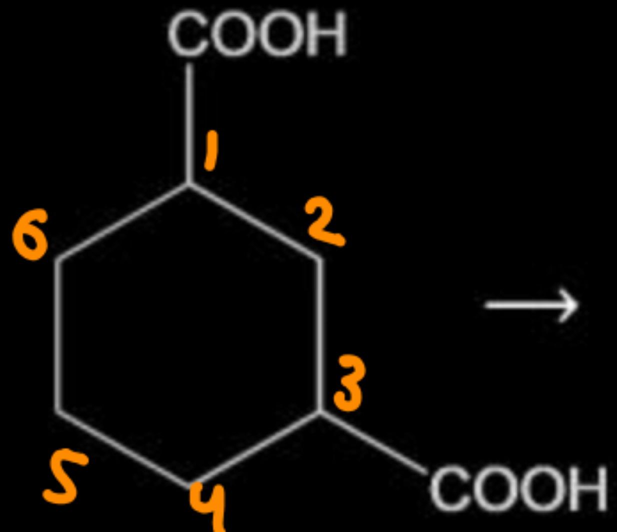
note → If terminating functional group is directly attatched to Ring then Ring is PCC.

6. 

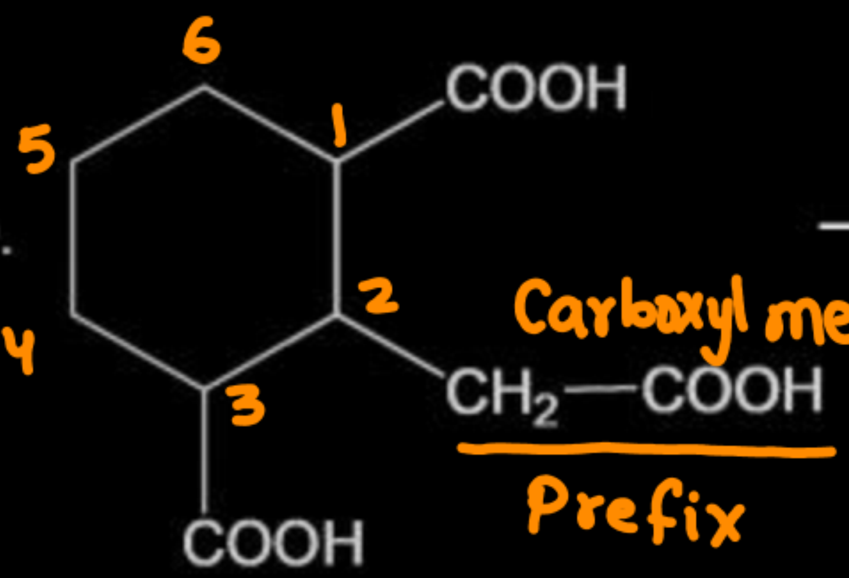
→ cyclopropane-1-carboxylic acid

7. 

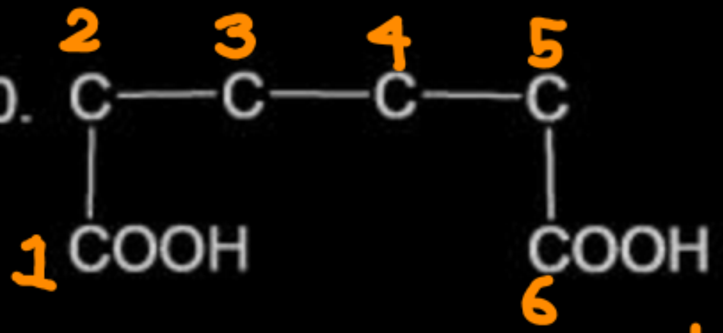
→ 2-cyclopropylethane-1-oic acid

8. 

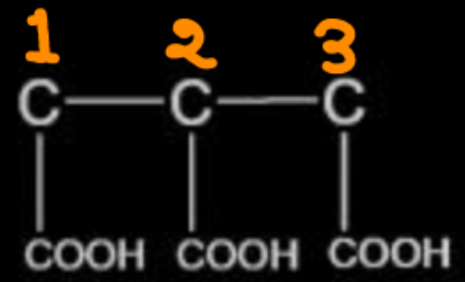
→ Cyclohexane-1,3-dicarboxylic acid

9. 

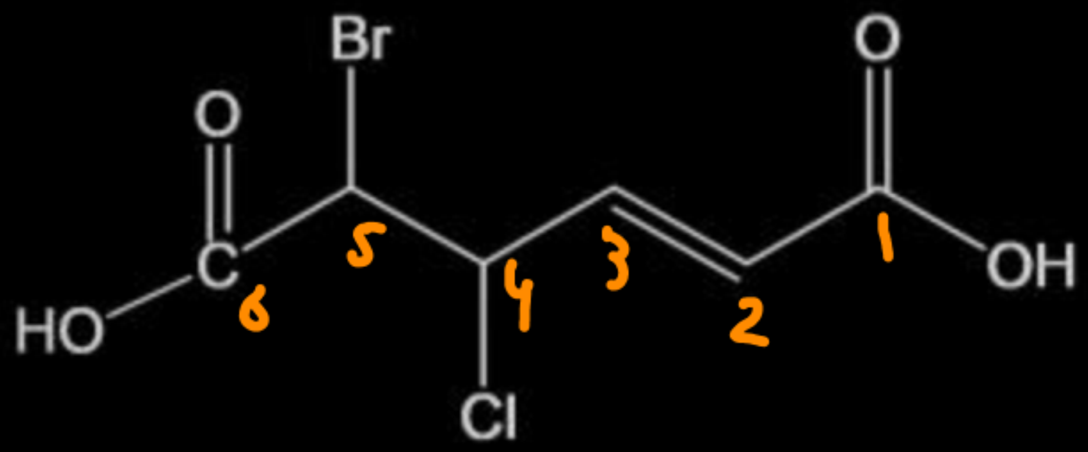
→ 2-Carboxymethylcyclohexane-1,3-dicarboxylic acid

10. 

→ Hexane-1,6-dioic acid

11. 

→ Propane-1,2,3-tricarboxylic acid

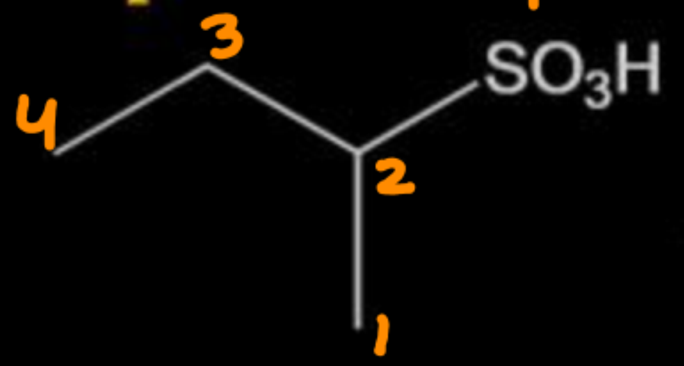
12. 

→ 5-Bromo-4-chlorohex-2-ene-1,6-dioic acid

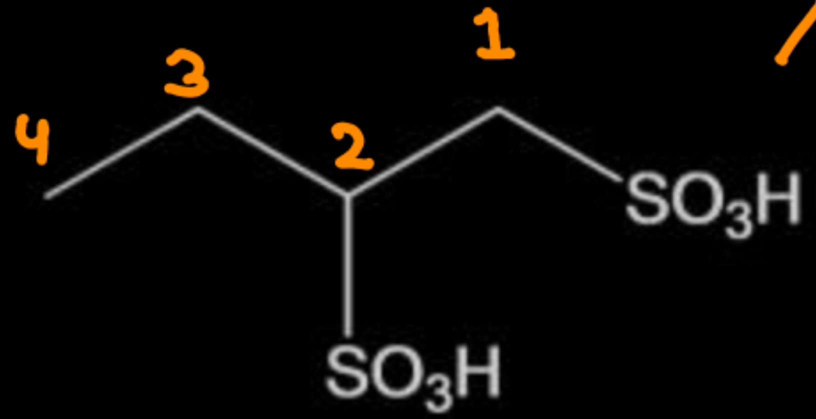
Sulphuric Acid

Examples:

2°suffix

1. 

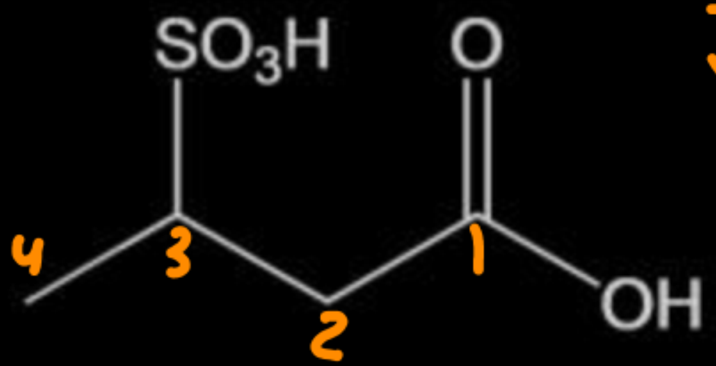
→ Butane-2-Sulphonic acid

2. 

→ Butane-1,2-disulphonic acid

Senior FG → 2°suffix
Junior FG → 2° Prefix

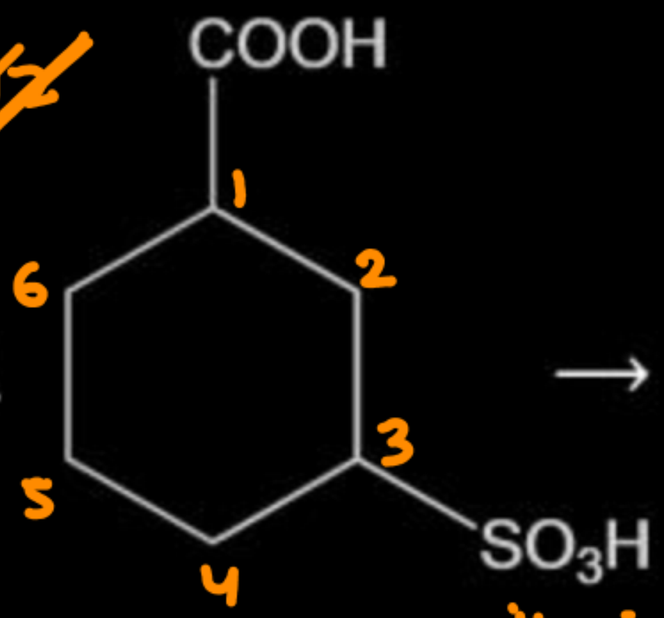
3-Sulphobutane-1-oicacid

3. 

→

2°
senior-suffix

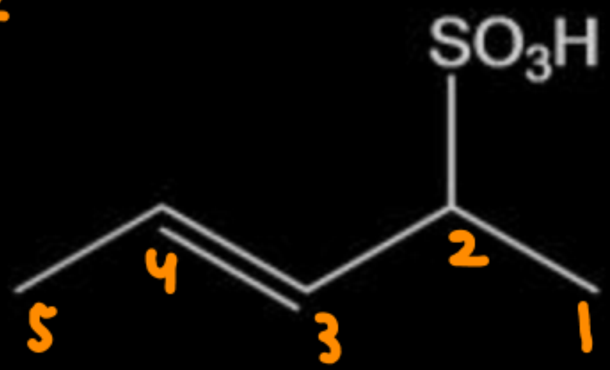
4.



junior→Prefix 2°

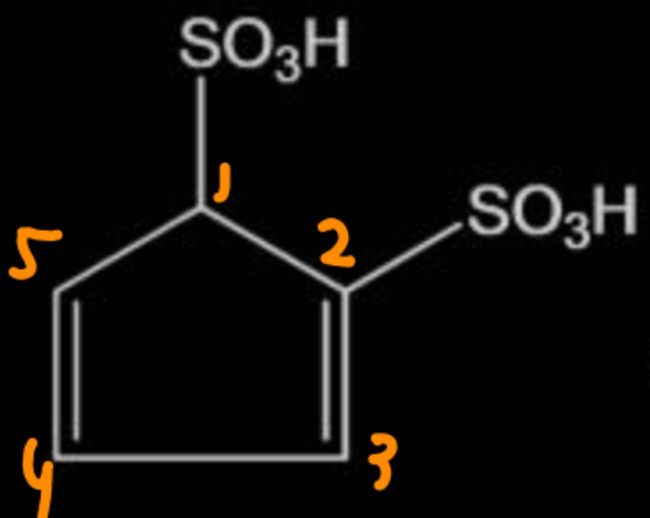
→ 3-sulphocyclohexane-1-carboxylic acid

5.



→ Pent-3-ene-2-sulphonic acid

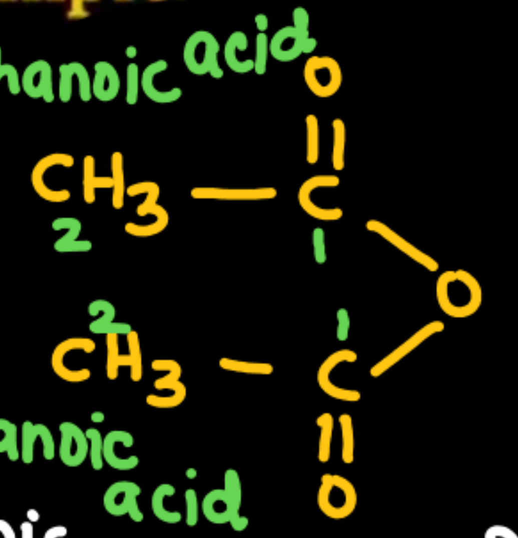
6.



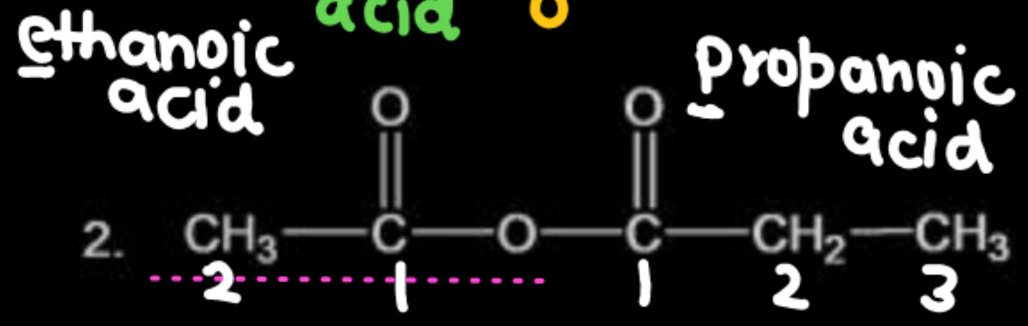
→ cyclopenta-2,4-diene-1,2-disulphonic acid

Acid Anhydride

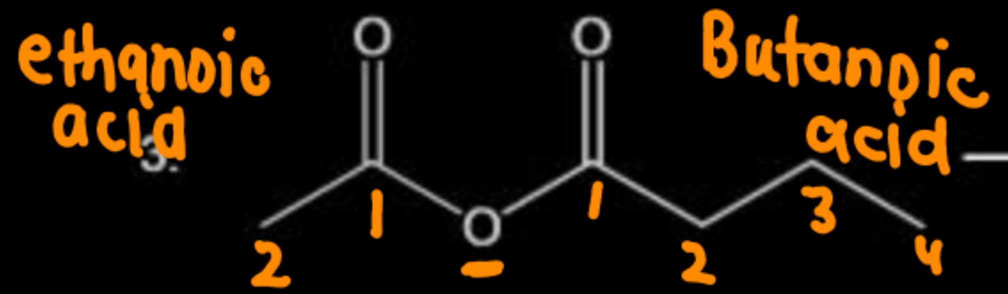
Examples:

1. 

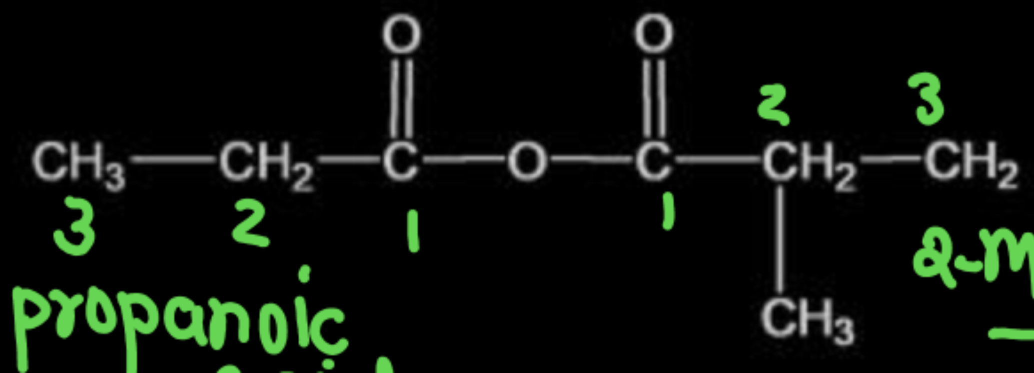
→ ethanoic anhydride

2. 

→ Ethanoic propanoic anhydride

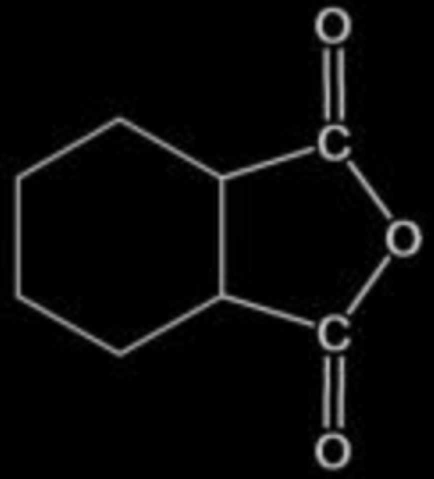
3. 

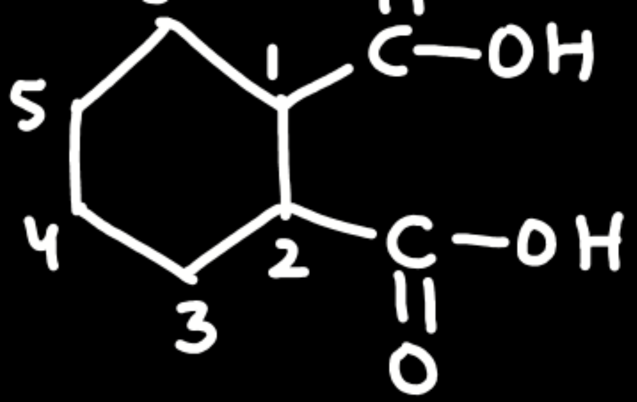
→ Butanoic ethanoic anhydride

4. 

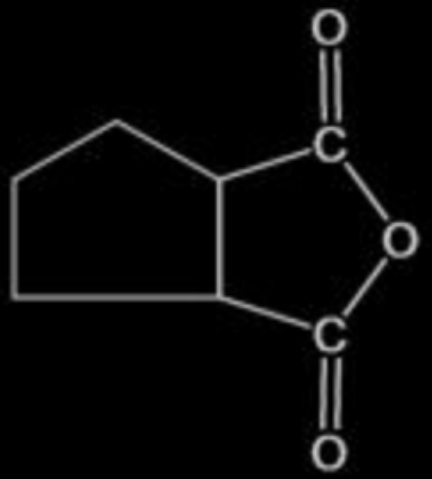
→ 2-methylpropanoicpropanoic anhydride

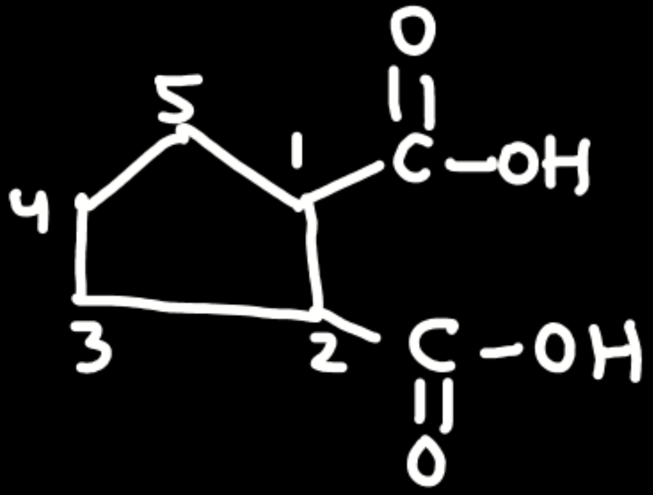
2-methylpropanoic acid

5. 



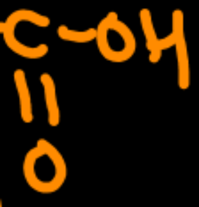
cyclohexane-1,2-dicarboxylic anhydride

6. 



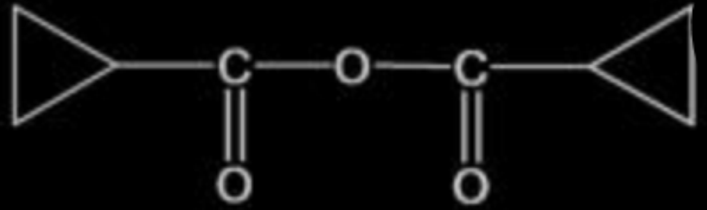
cyclopentane-1,2-dicarboxylic anhydride

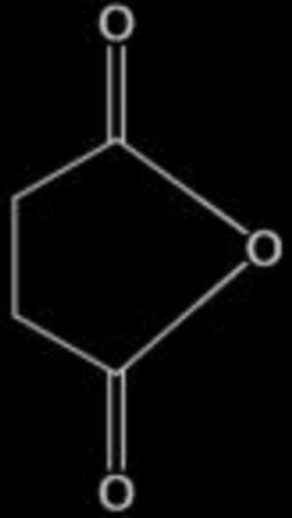
cyclopropane-1-carboxylic anhydride

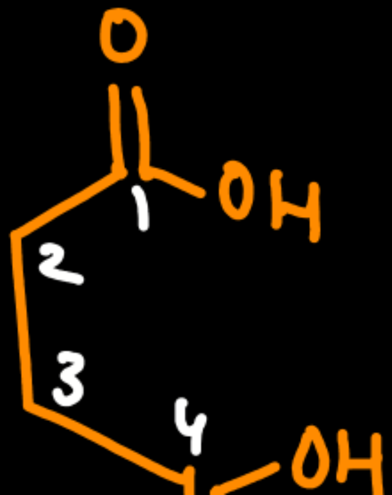


pane

xylic

7. 

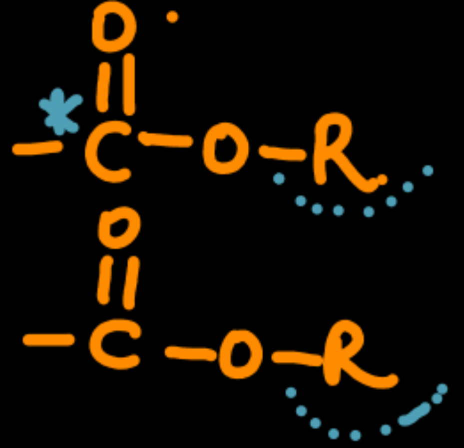
8. 



But-1,4-dioic anhydride

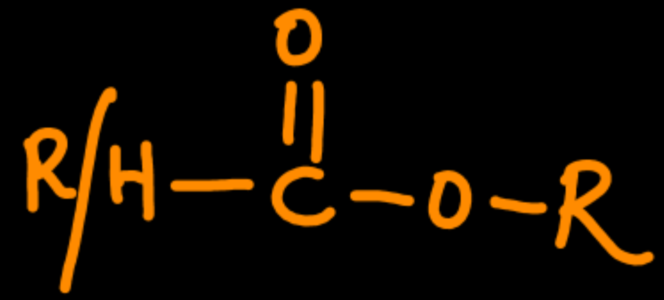
Ester

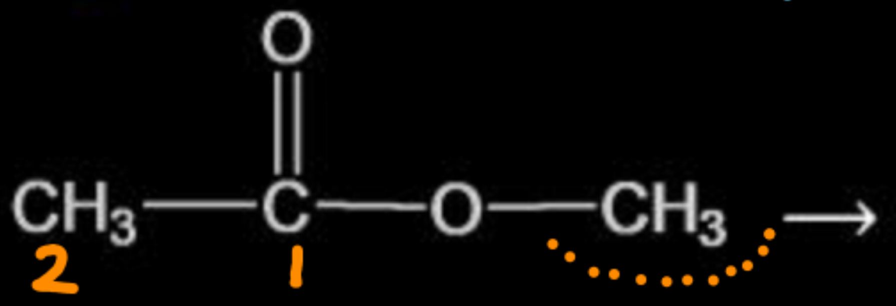
Examples:

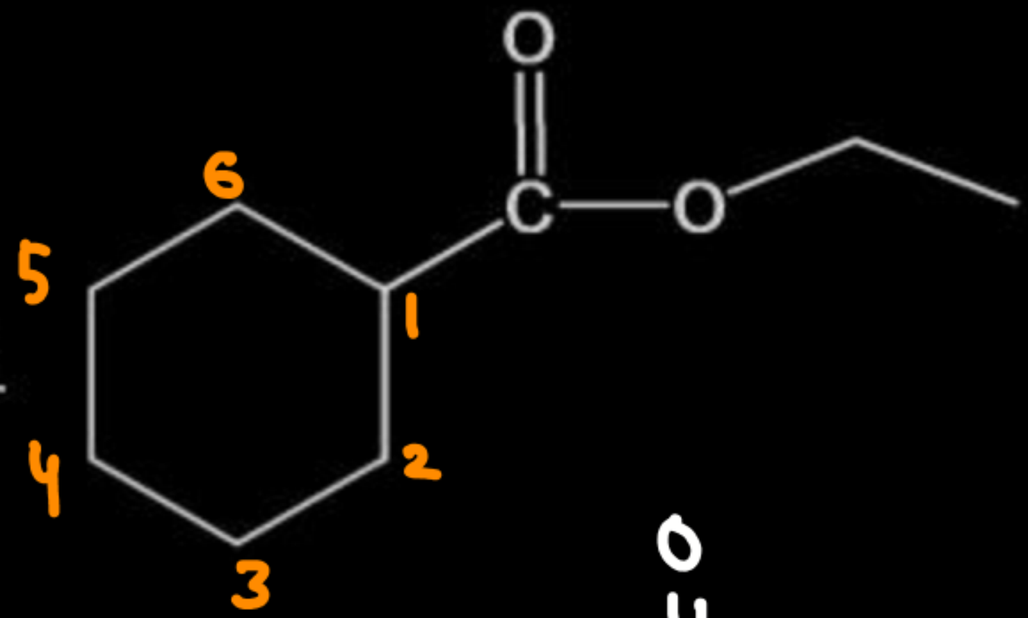


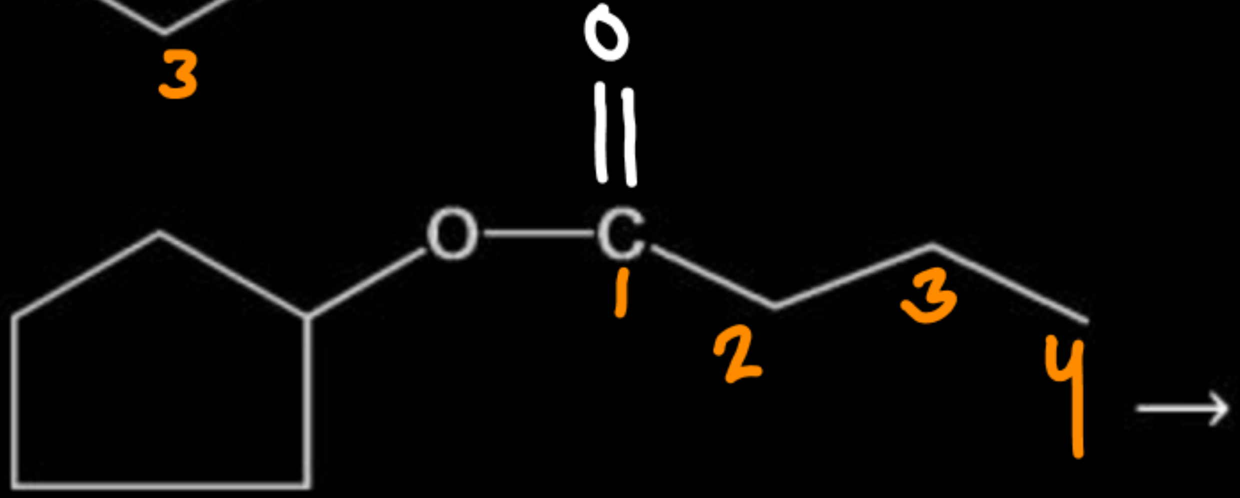
Alkyl Alkanoate

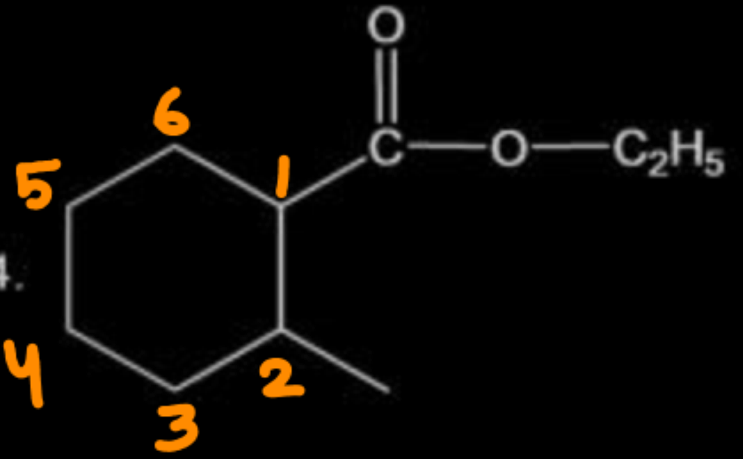
Alkyl Alkane Carboxylate



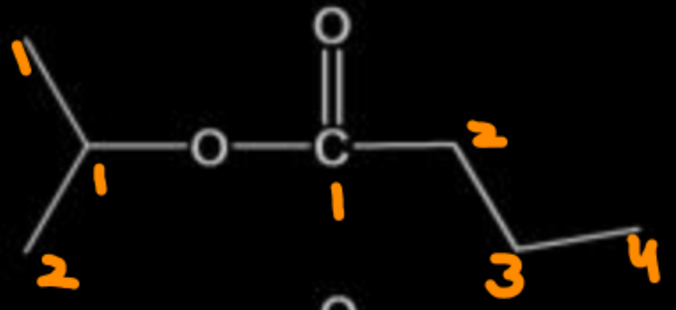
1.  Methyl ethanoate

2.  → Ethyl cyclohexanecarboxylate

3.  cyclopentyl butanoate

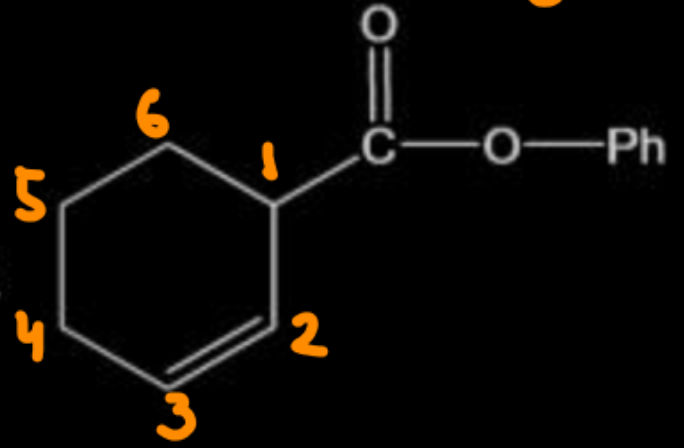
4. 

→ Ethyl-2-methylcyclohexanecarboxylate

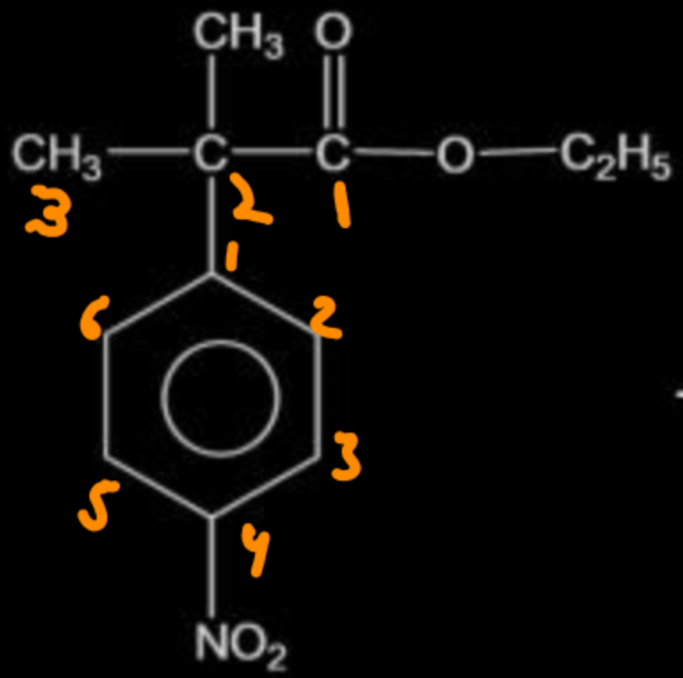
5. 

→ Isopropylbutanoate

1-methylethylbutanoate

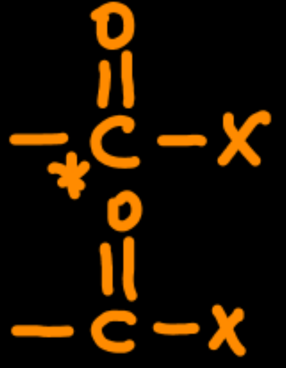
6. 

→ Phenyl cyclohex-2-enecarboxylate

7. 

→ Ethyl-2-methyl-2-(4-nitrophenyl)propanoate

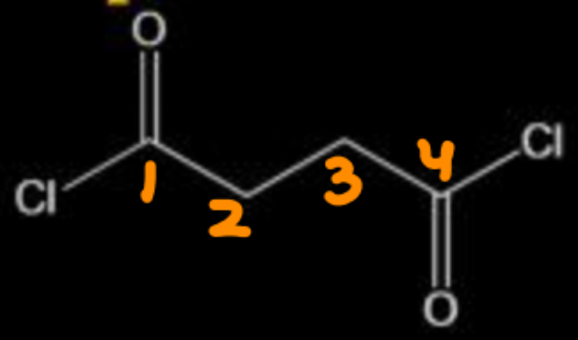
Acid Halide

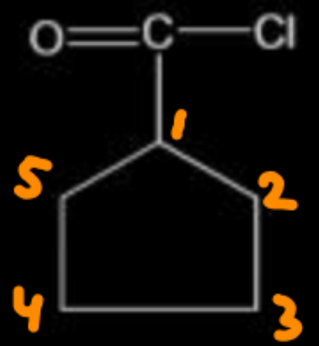


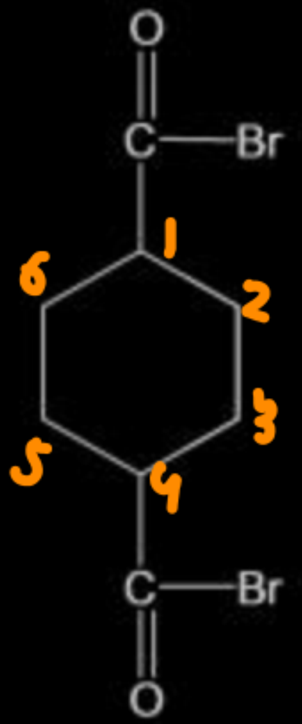
oyl halide

Carbonyl halide

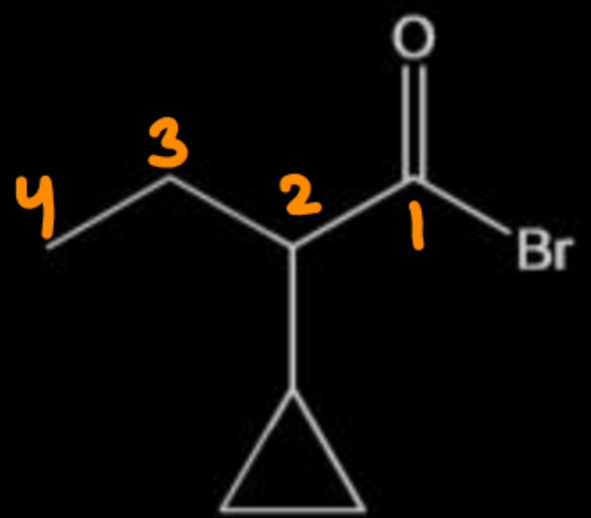
Examples:

1.  → Butane-1,4-dioylchloride

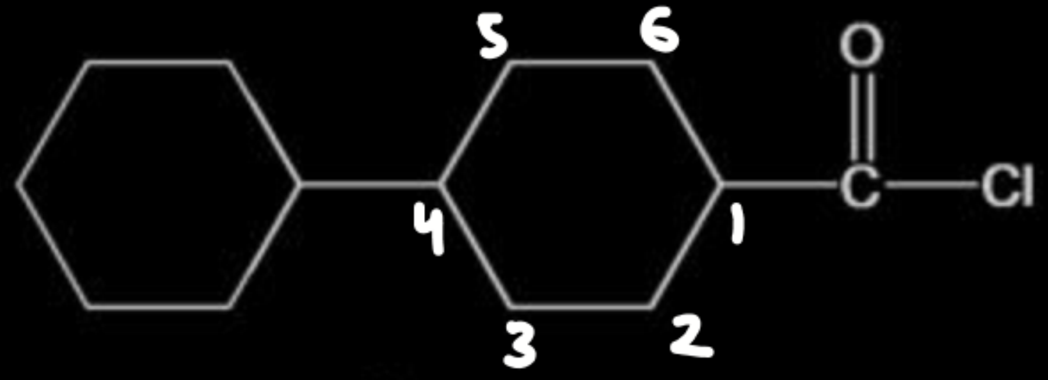
2.  → cyclopentane-1-carbonylchloride

3.  → cyclohexane-1,4-dicarbonylbromide

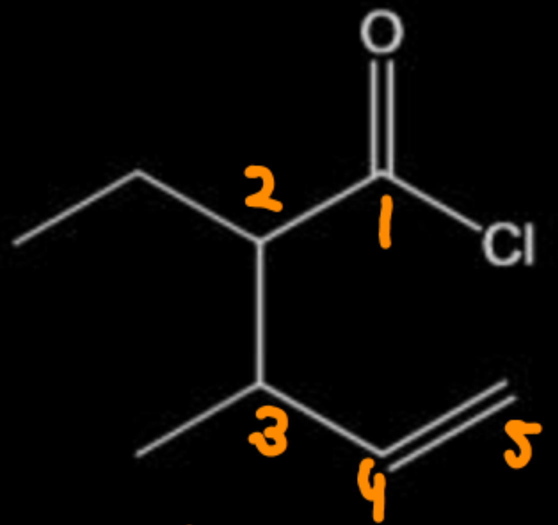
FMCB

4. 

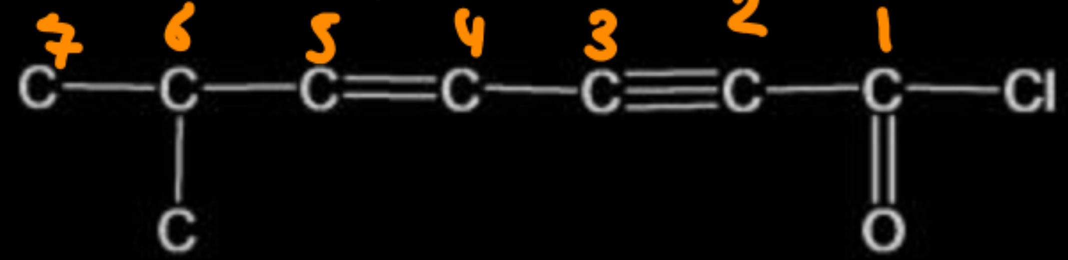
→ 2-cyclopropylbutane-1-oylbromide

5. 

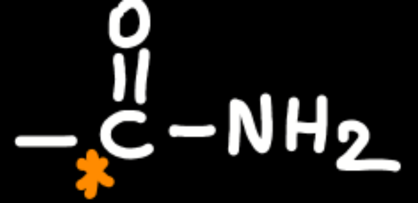
→ 4-cyclohexylcyclohexane-1-carbonylchloride

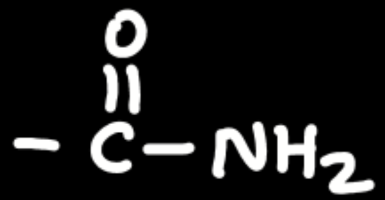
6. 

→ 2-ethyl-3-methylpent-4-ene-1-oylchloride

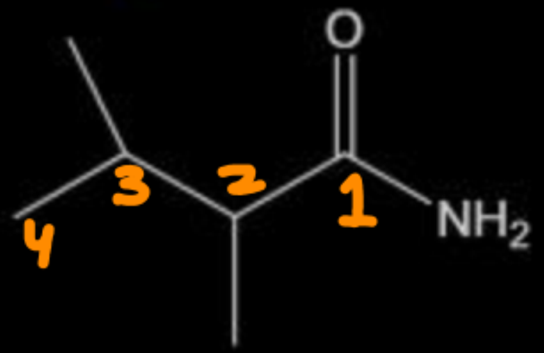
7. 

→ 6-methylhept-4-ene-2-yne-1-oylchloride

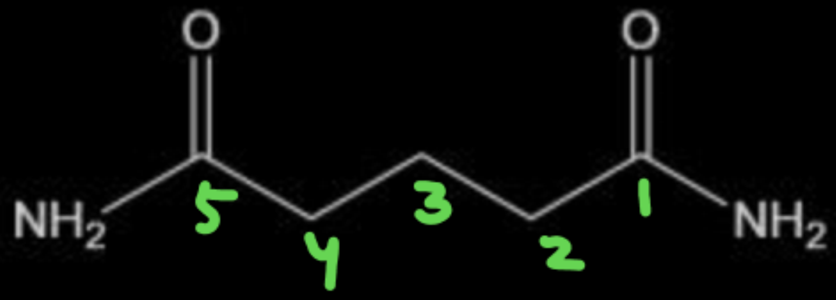
Amide  amide

Examples:  Carboxamide

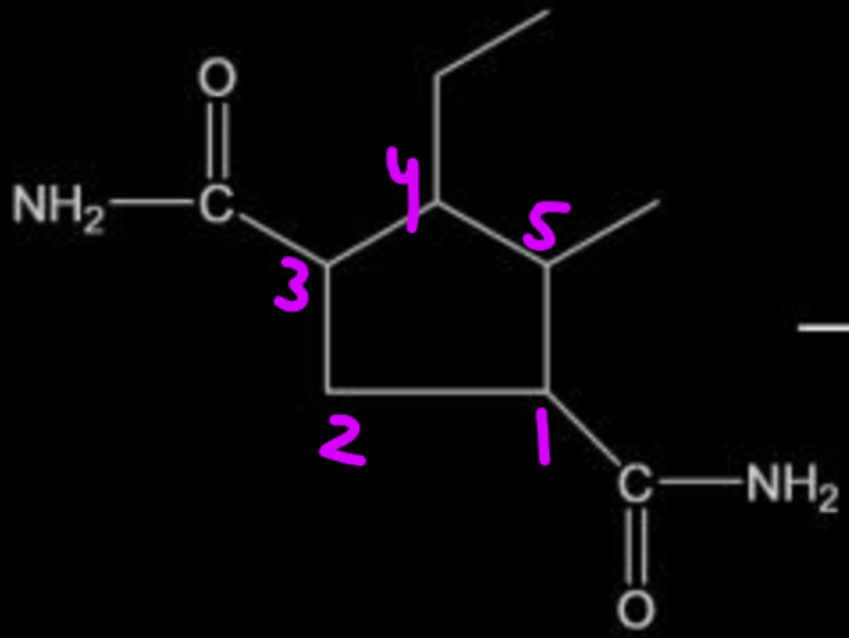
Prefix → carbamoyl

1. 

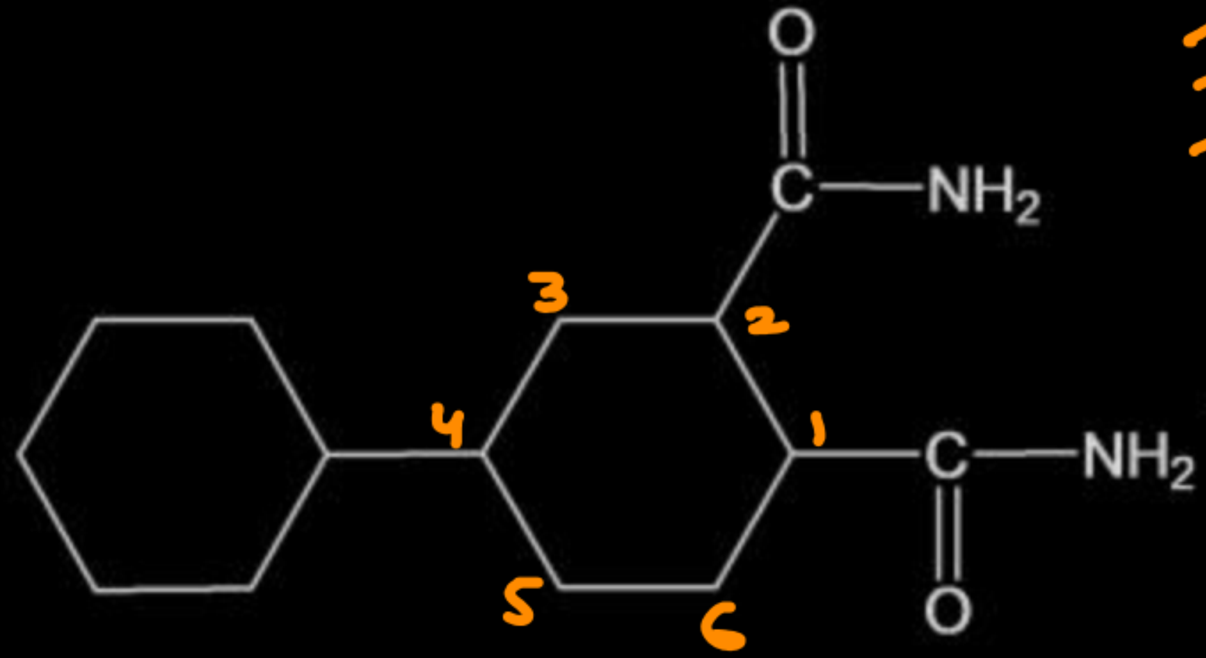
→ 2,3-dimethylbutane-1-amide

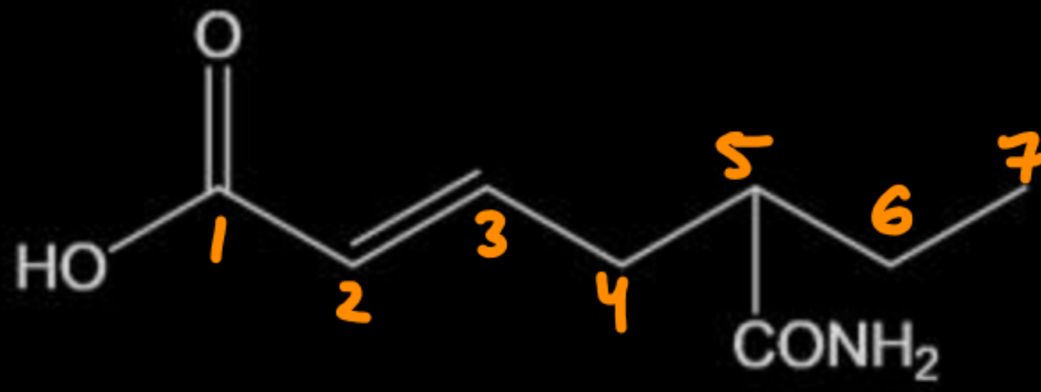
2. 

→ Pentane-1,5-diamide

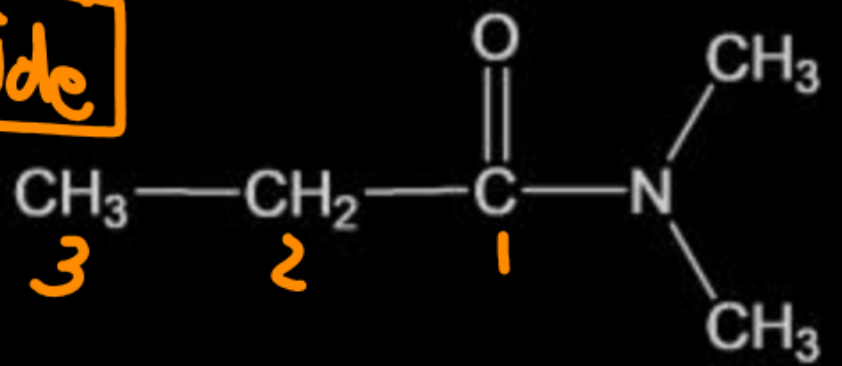
3. 

→ 4-ethyl-5-methylcyclopentane-1,3-dicarboxamide

4.  → 4-cyclohexylcyclohexane-1,2-dicarboxamide

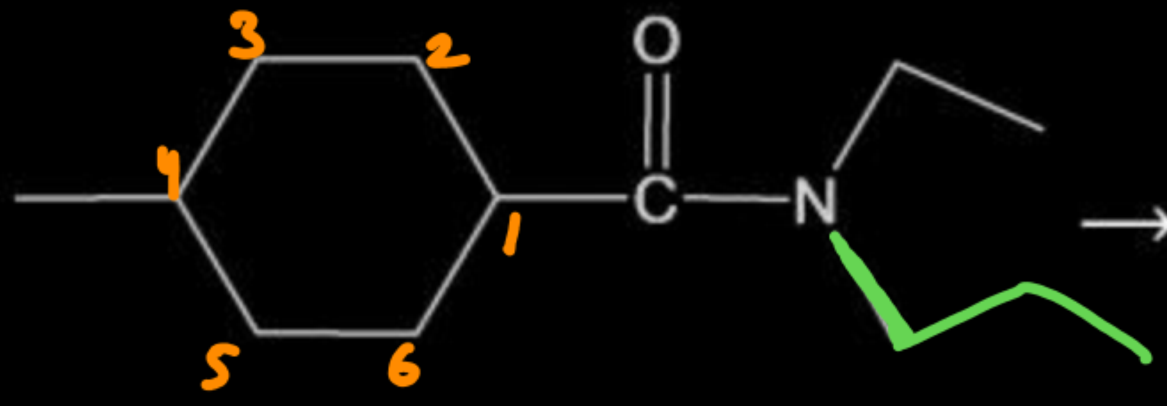
5.  → 5-Carboamoylhept-2-ene-1-oicacid

3° amide

6.  → N,N-dimethylpropane-1-amide

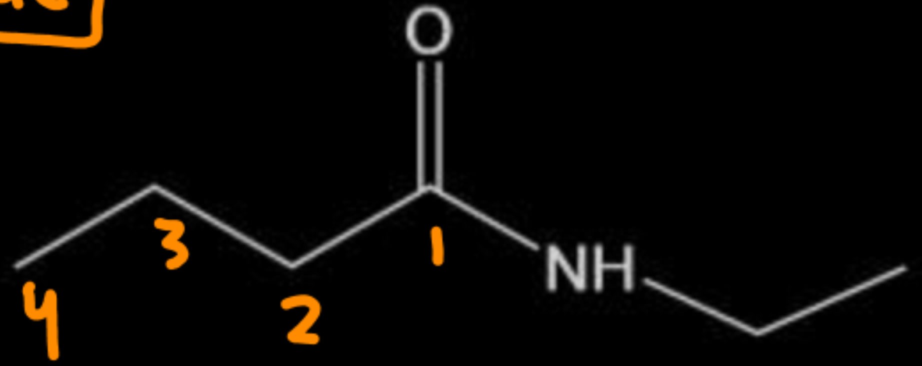
3° amide

~~2~~1012

7. 

→ N-ethyl-N-propyl-4-methylcyclohexane-1-carboxamide

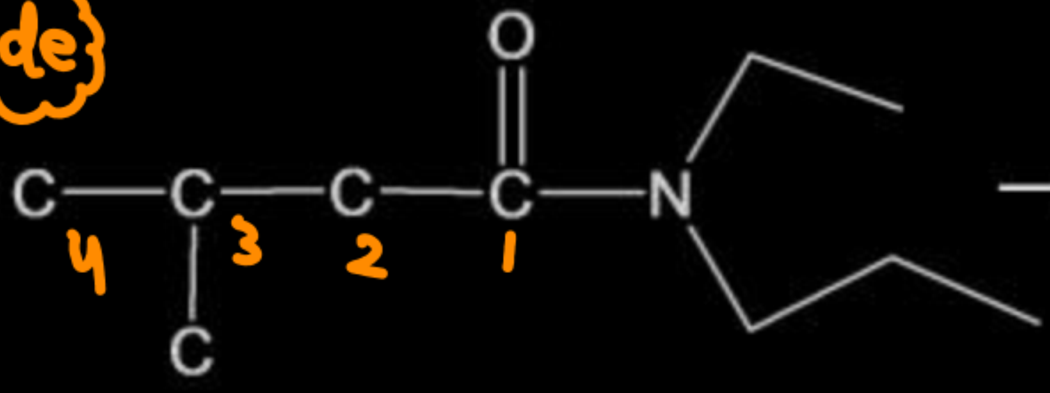
2° amide

8. 

→ N-ethylbutan~~e~~-1-amide

~~2~~ ~~1012~~ 2

3° amide

9. 

→ N-ethyl-N-propyl-3-methylbutan~~e~~-1-amide

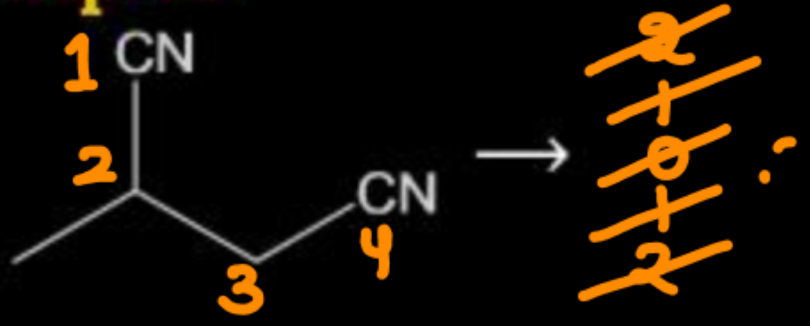
Cyanide (CN)

$-C\equiv N$ * nitrile

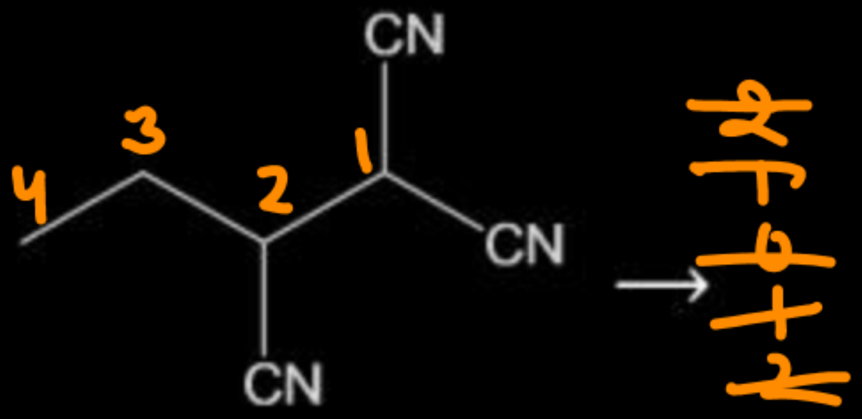
$-C\equiv N$ Carbonitrile

cyano

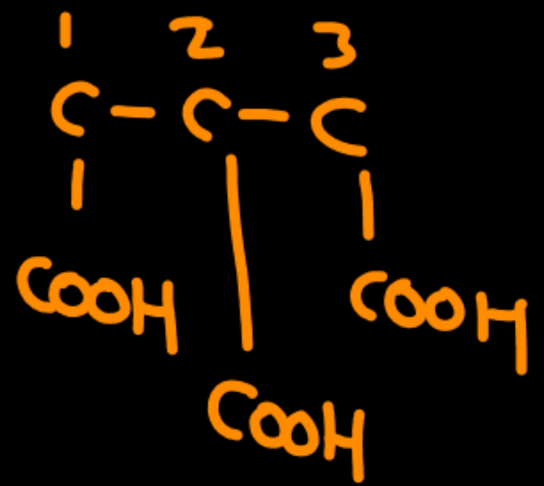
Examples:

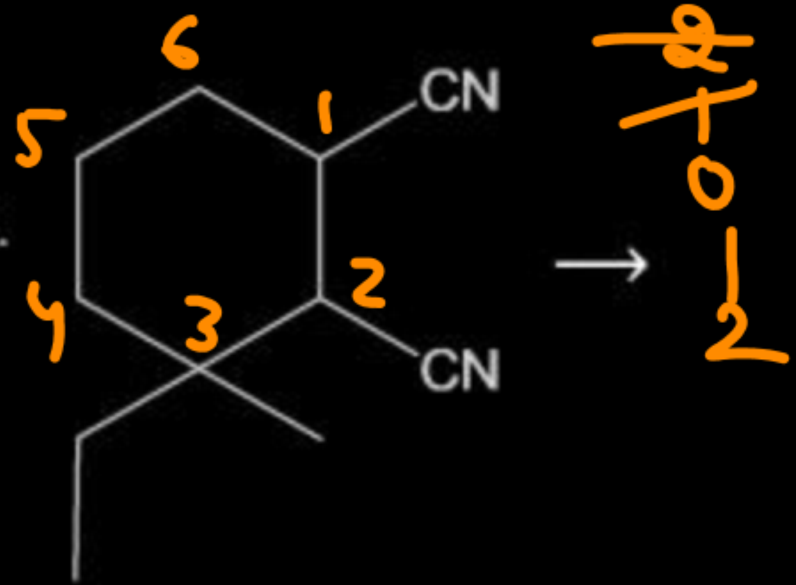
1. 

2-methylbutane-1,4-dinitrile

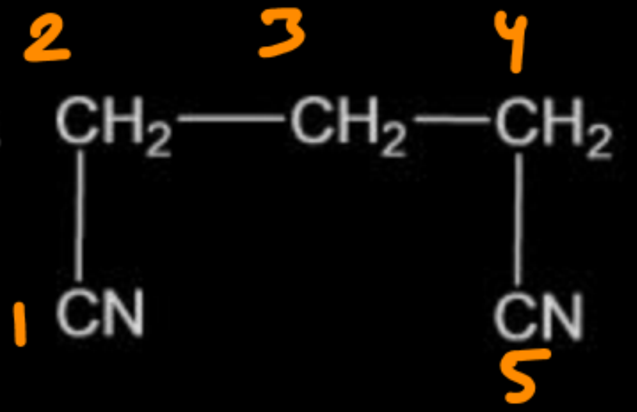
*2. 

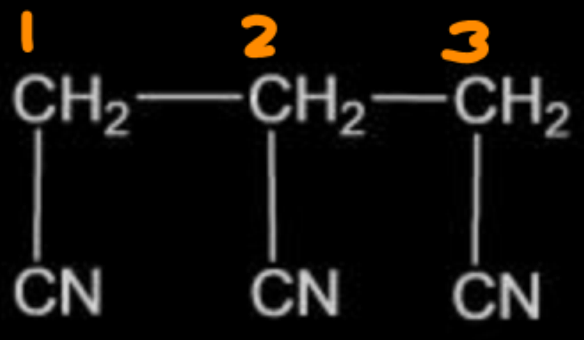
Butane-1,1,2-tricarbonitrile

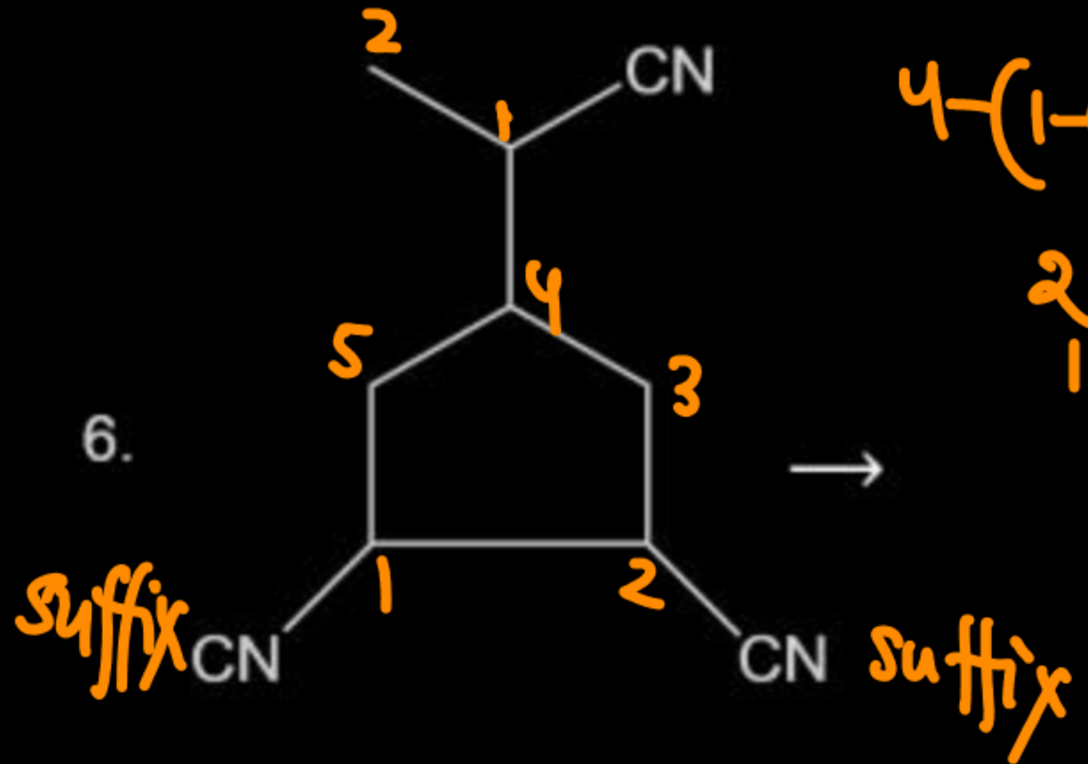


3. 

3-ethyl-3-methylcyclohexane-1,2-dicarbonitrile

4.  → Pentane-1,5-dinitrile

5.  → Propane-1,2,3-tricarbonitrile

6.  → 4-(1-cyanoethyl)cyclopentane-1,2-dicarbonitrile

Isocyanide/Isonitrile (−N≡C)

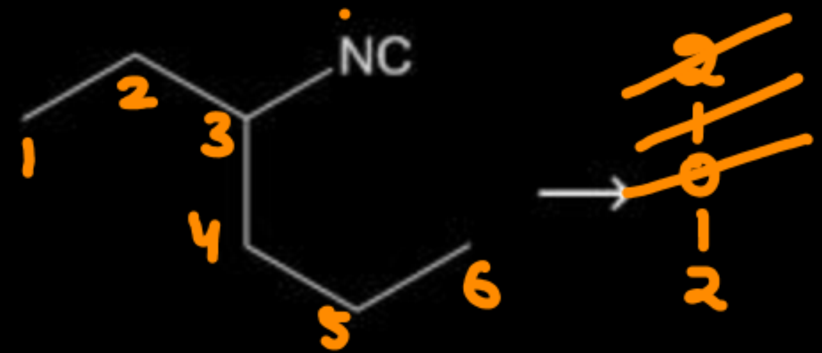
Suffix

−N≡C → isonitrile/Carbylamine

Prefix

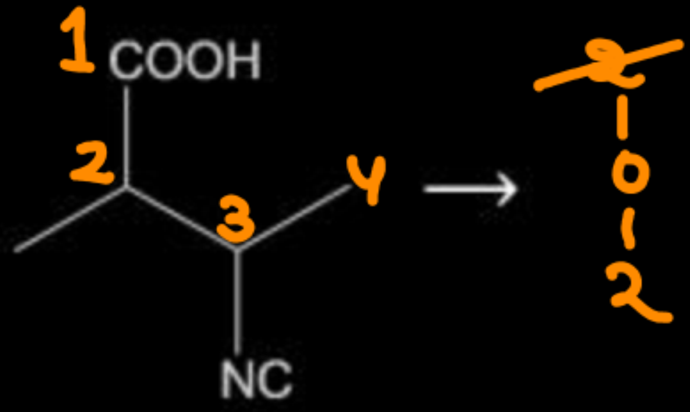
Isocyano/Carbylamino

2.



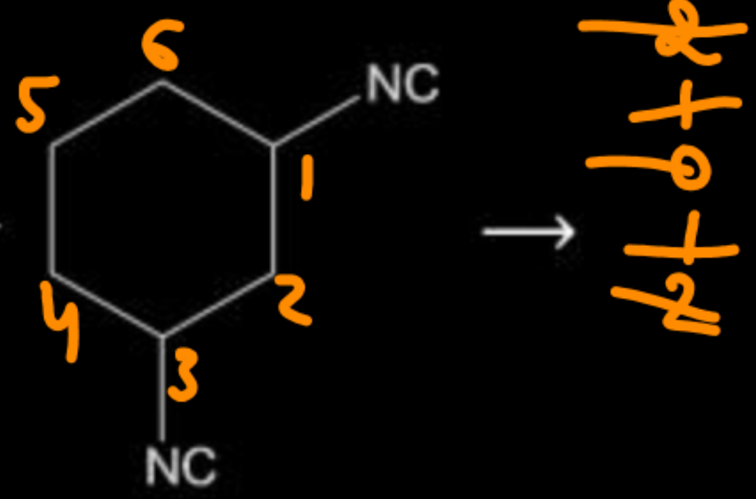
Hexan~~e~~-3-isonitrile

3.



3-isocyano-2-methylbutan~~e~~-1-oicacid

4.



Cyclohexane-1,3-diisonitrile

Aldehyde – (CHO)

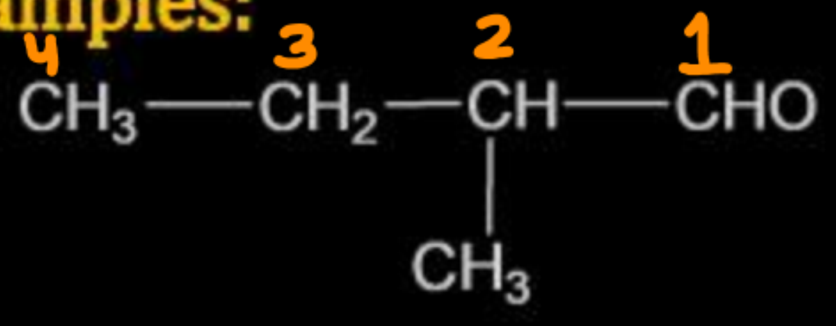
–C(=O)–H → al

–C(=O)–H → Carbaldehyde

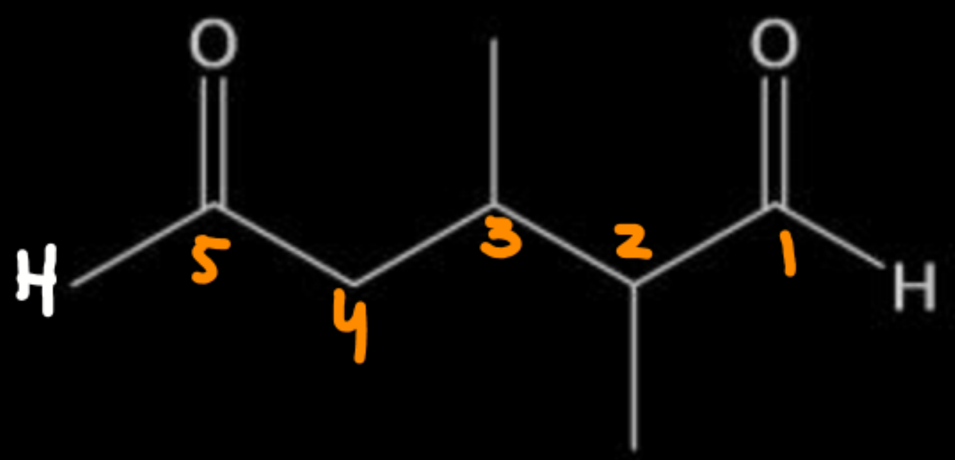
Prefix → formyl → when C is not counted

→ oxo → when C is counted

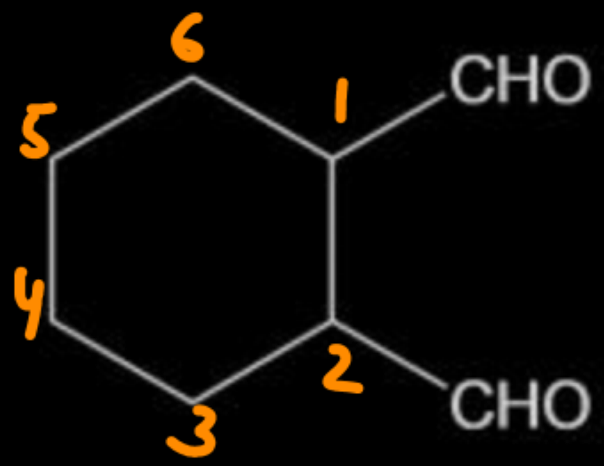
Examples:

1. 

→ 2-methylbutane-1-al

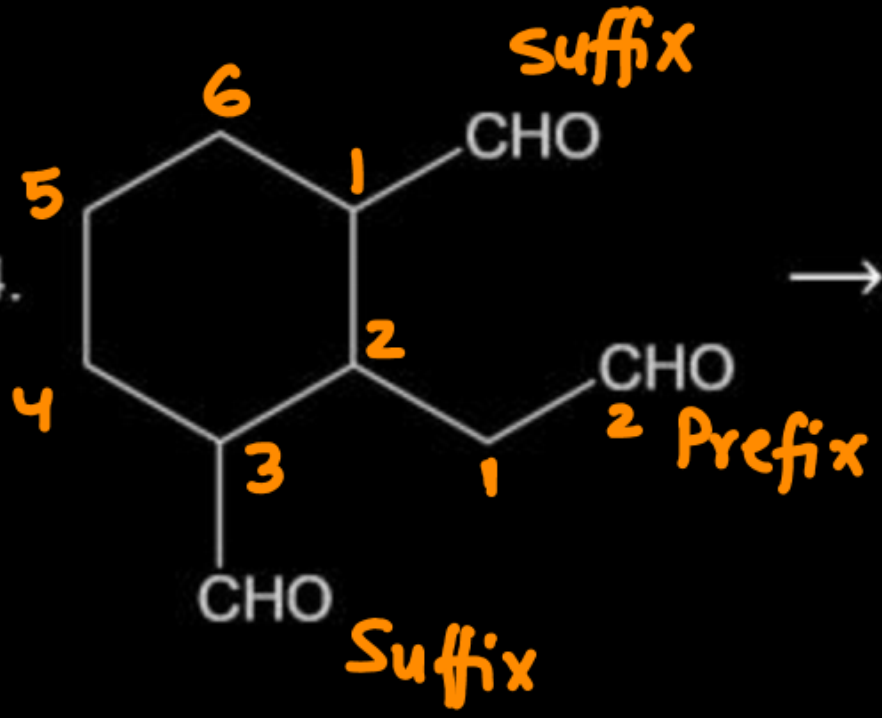
2. 

→ 2,3-dimethylpentane-1,5-dial

3. 

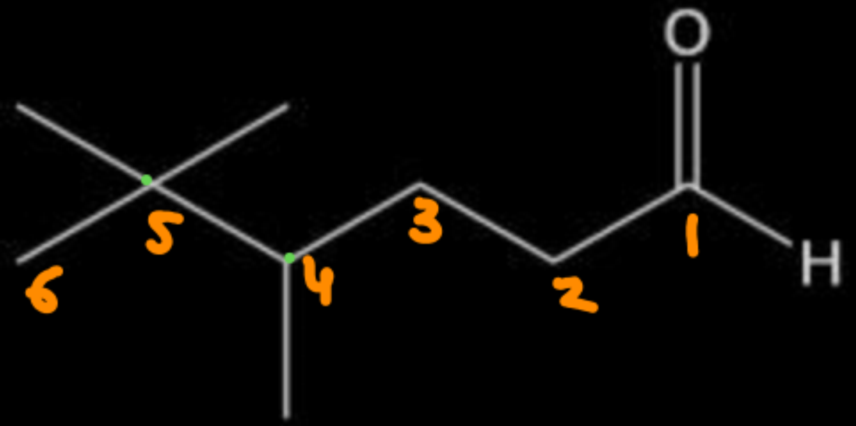
→ cyclohexane-1,2-dicarbaldehyde

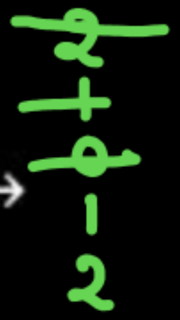
when C of CHO is not Counted
↓

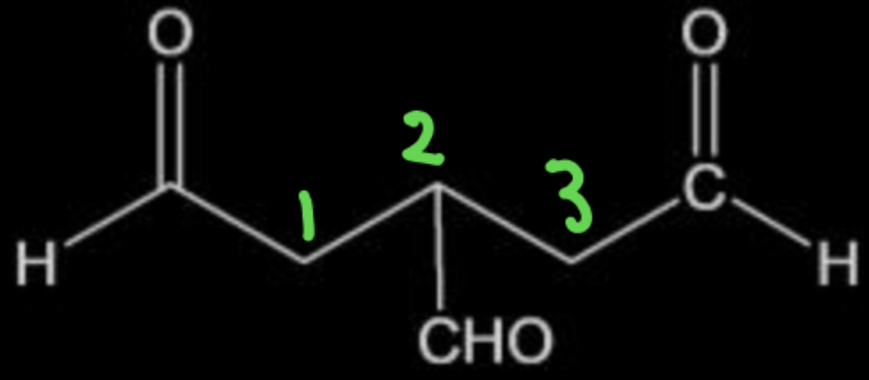
4. 

→ 2-formylmethylcyclohexane-1,3-dicarbaldehyde

2-oxoethylcyclohexane-1,3-dicarbaldehyde
↑
C of CHO is counted.

5. 

→  4,5,5-trimethylhexan~~e~~-1-al

6. 

→  Propane-1,2,3-tricarbaldehyde

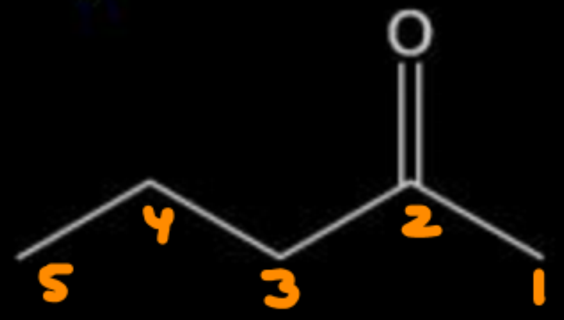


Suffix
one

Prefix
oxo/Keto ✓

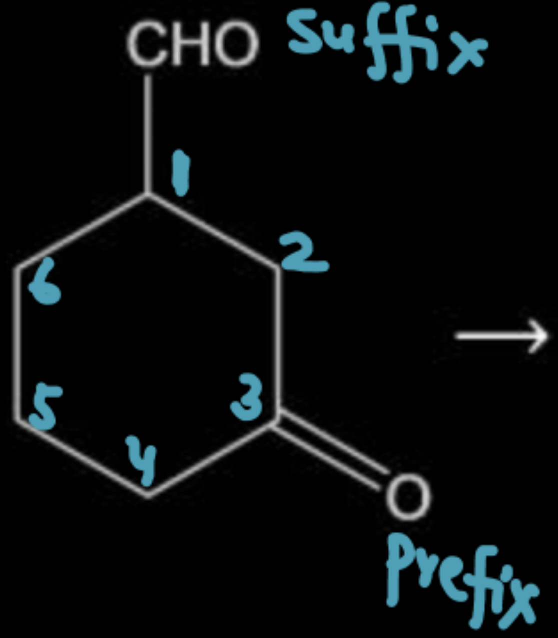
Ketone

Examples:

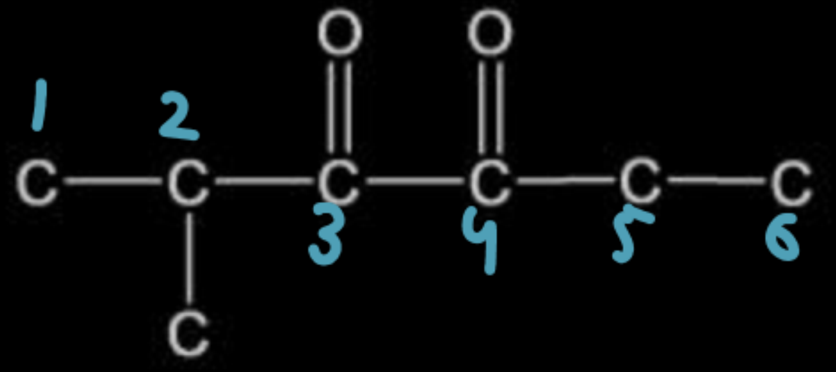
1. 

→ 

Pentan~~e~~-1-one

2. 

→ 3-oxocyclohexane-1-Carbaldehyde
3-keto cyclohexane-1-Carbaldehyde

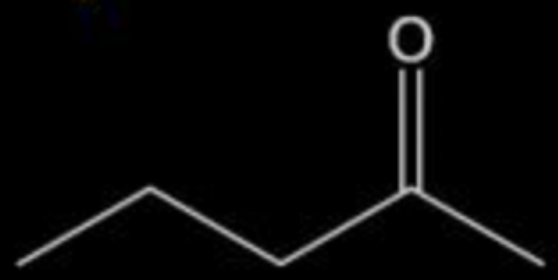
3. 

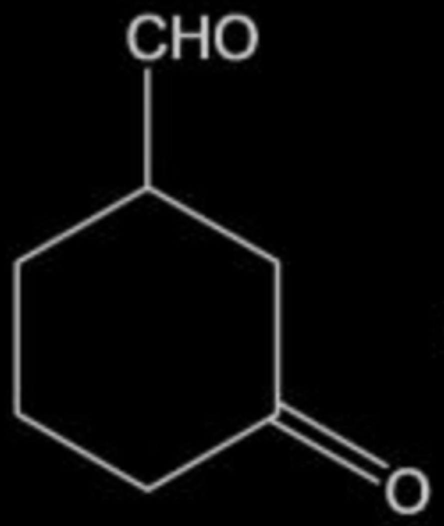
→ 

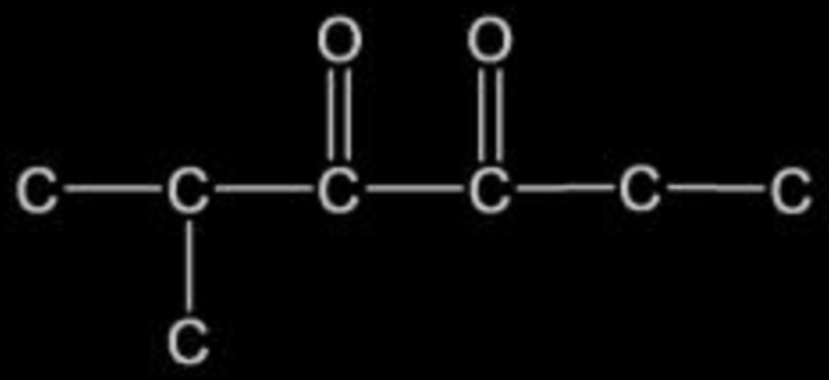
2-methylhexane-3,4-dione

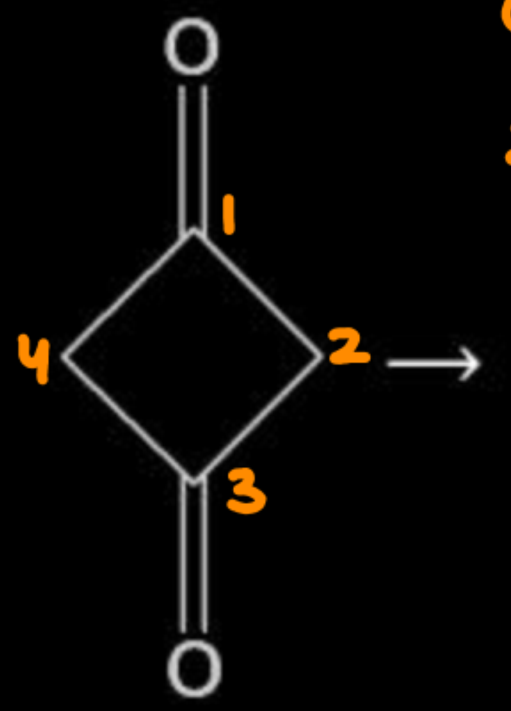
Ketone

Examples:

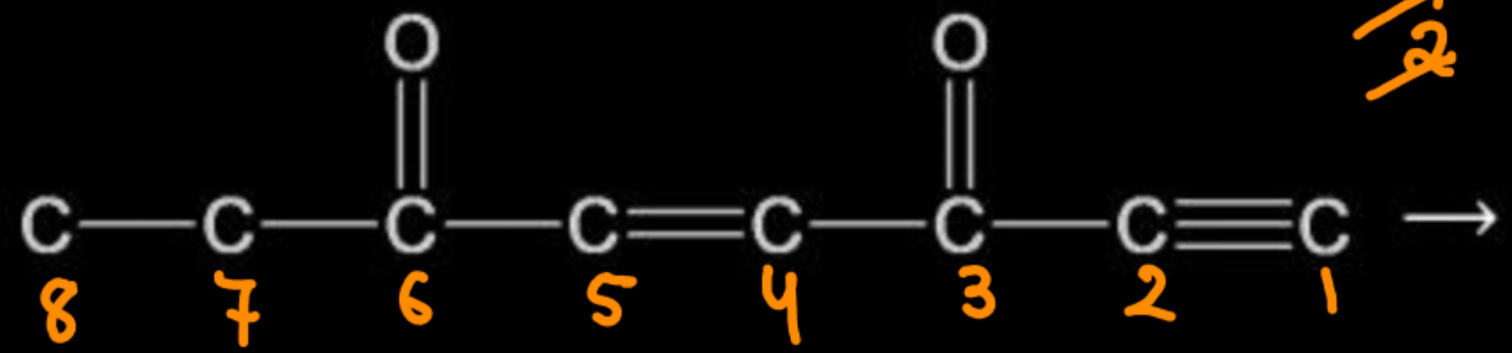
1.  →

2.  →

3.  →

4. 

Cyclobutane-1,3-dione

5. 

oct-4-ene-1-yne-3,6-dione

13 FG

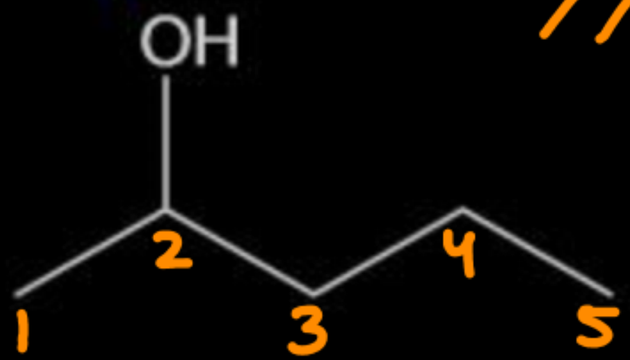
acid or acid derivative 6:

1) COOH
2) SO_3H
3) -COOOC-
4) COOR
5) COX
6) $CONH_2$

7) -CN
8) -NC
9) -CHO
10) -CO-
11) -OH
12) -SH
13) $-NH_2$

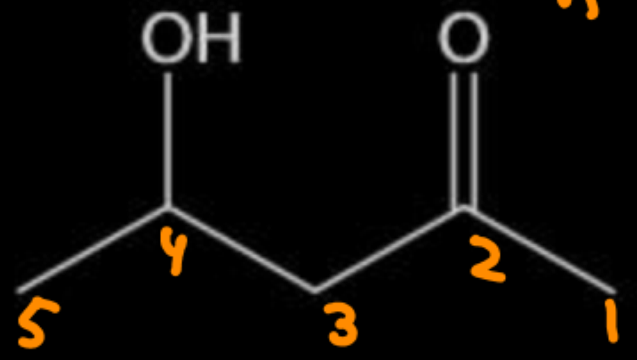
Alcohol

Examples:

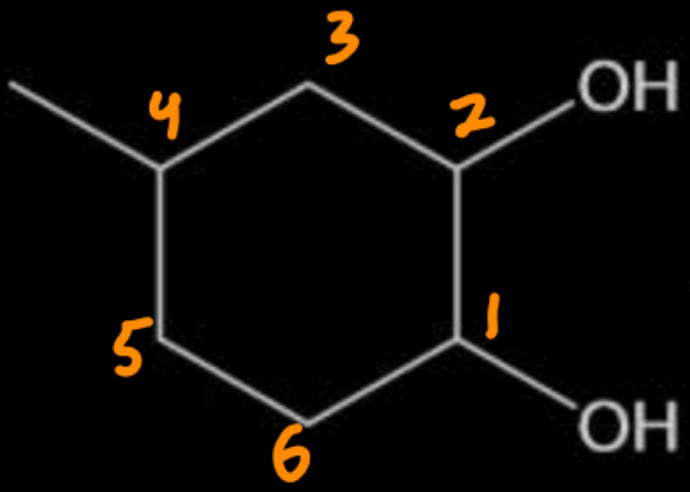
1. 

→ Pentane-2-ol

Prefix suffix

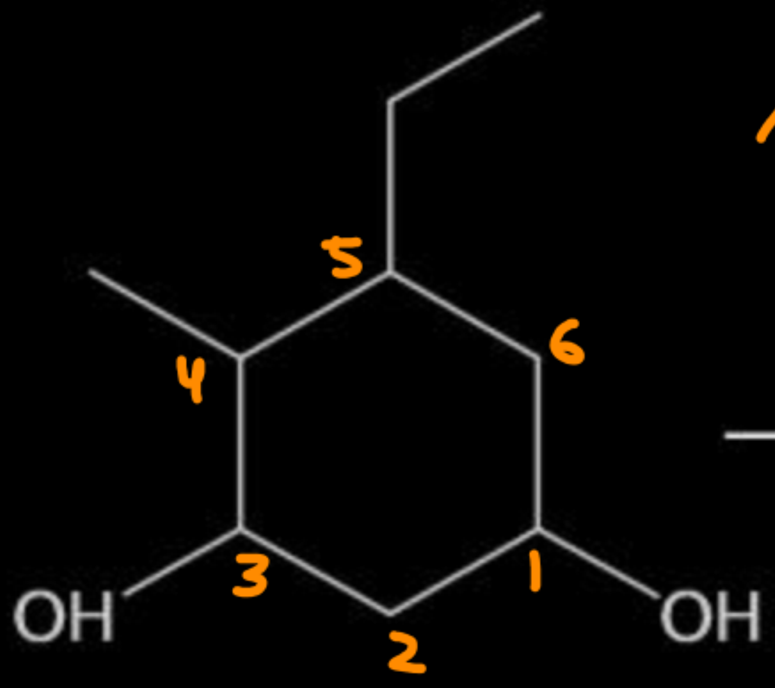
2. 

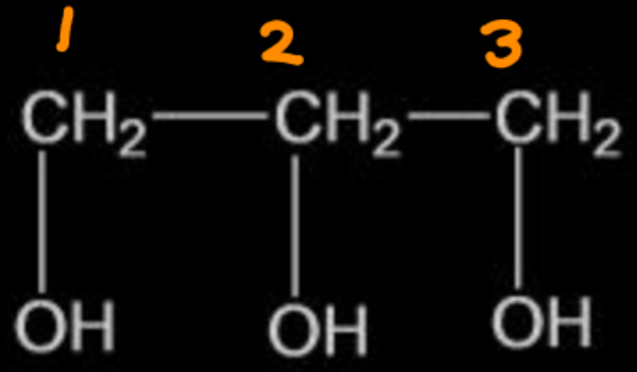
→ 4-Hydroxypentane-2-one

3. 

→ 4-methylcyclohexane-1,2-diol

FMCB

4.  → 5-ethyl-4-methylcyclohexane-1,3-diol

5.  → Propane-1,2,3-triol

-SH → Suffix → thiol

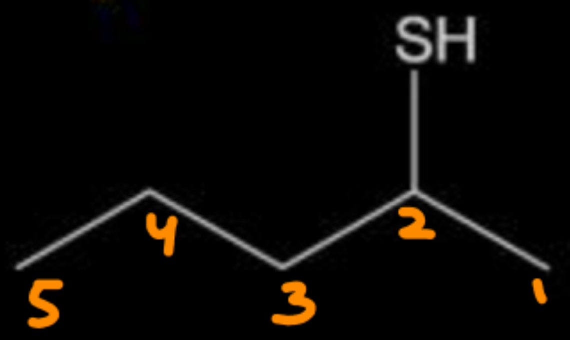
-SH → Prefix → Mercepto

Thio-alcohol

Examples:

2/1012

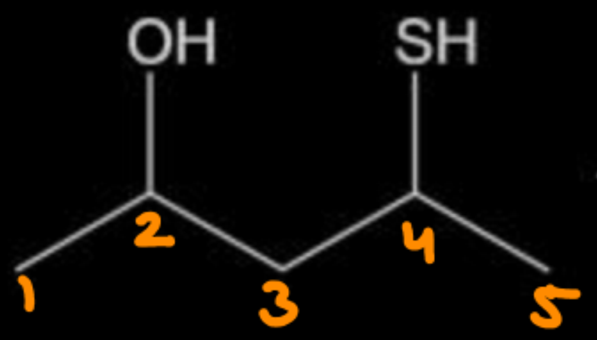
1.



→ Pentane-2-thiol

2/012

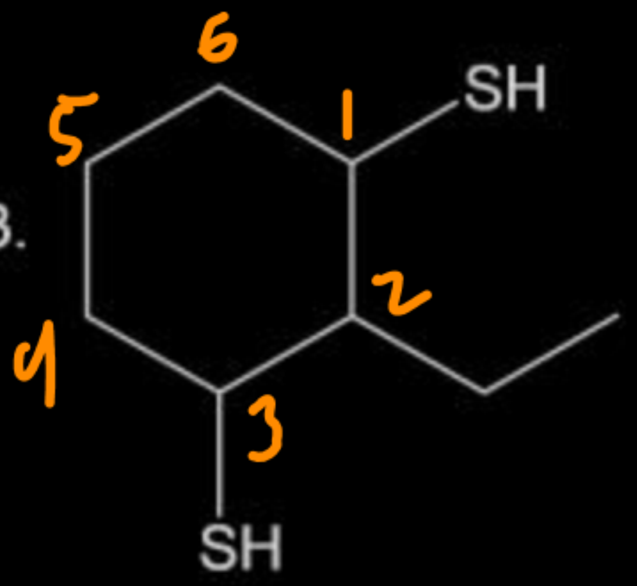
2.



→ 4-merceptopentane-2-ol

2!012

3.



→ 2-ethylcyclohexane-1,3-dithiol

$-NH_2 \rightarrow$ Suffix $\rightarrow$ amine

$-NH_2 \rightarrow$ Prefix $\rightarrow$ amino

Amine

Examples:

1. $CH_3—CH_2—CH_2—NH_2 \rightarrow$ Propane-1-amine (e struck out) Propanamine

(carbons numbered 3, 2, 1)

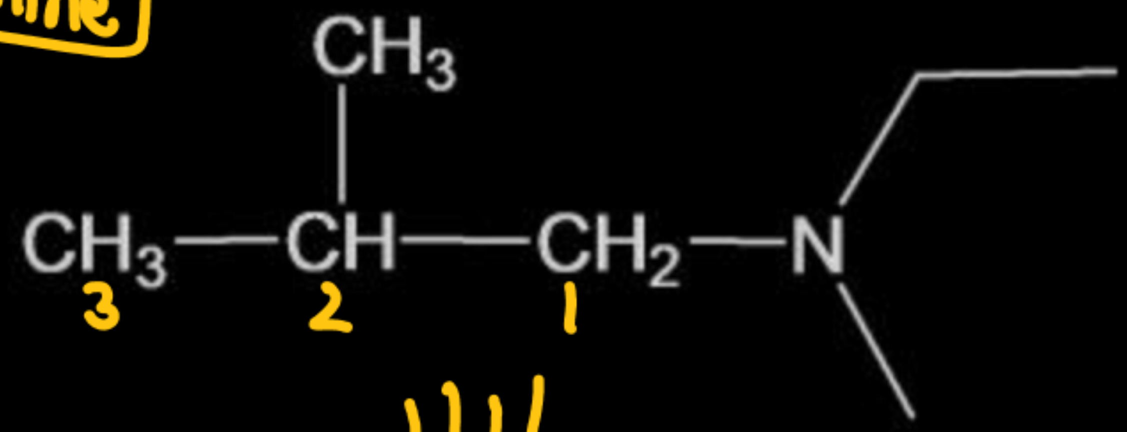
2° amine

2. $CH_3—CH_2—CH_2—NH—C_2H_5 \rightarrow$ N-ethyl propane-1-amine (e struck out)

(carbons numbered 3, 2, 1)

3° amine

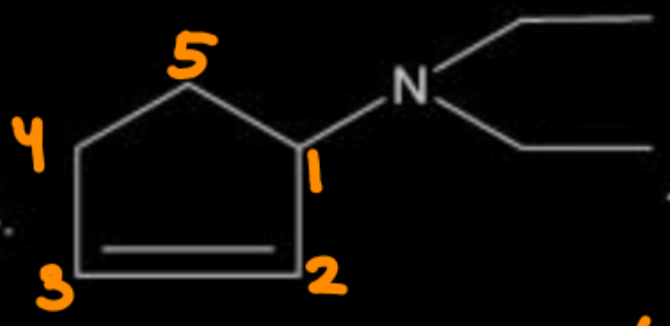
3.

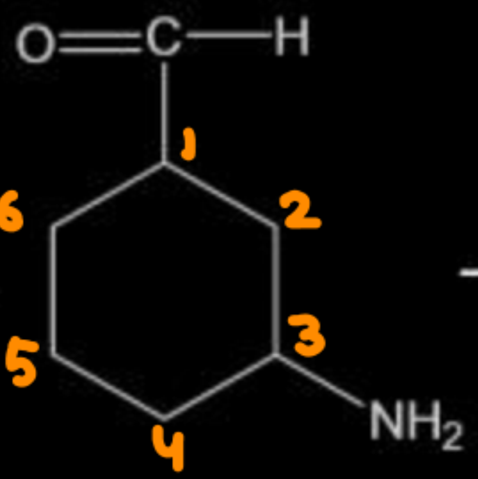


N-ethyl-N-methyl-2-methylpropane-1-amine

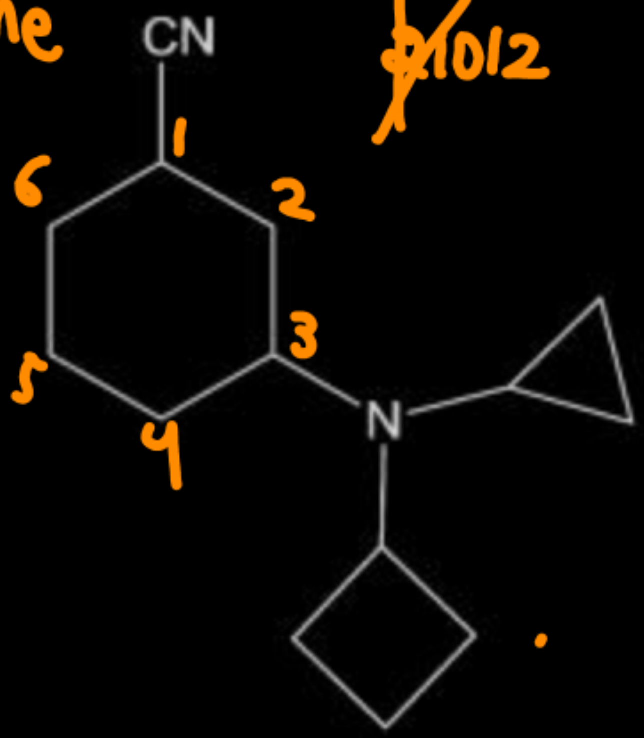
$\rightarrow$ N-ethyl-N,2-dimethylpropane-1-amine

3° amine

4.  → N,N-diethylcyclopent-2-en~~e~~-1-amine

5.  → 3-aminocyclohexane-1-carbaldehyde

3° amine

6.  → 3-(N-cyclobutyl-N-cyclopropylamino)cyclohexane-1-carbonitrile

Ether

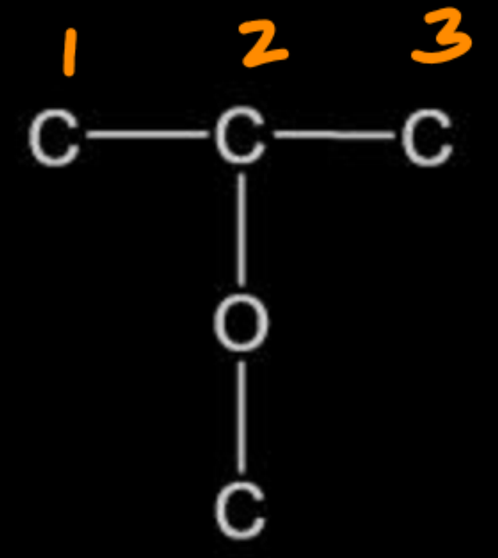
—O— → It is always treated as Prefix. (Sidechain/Branch)

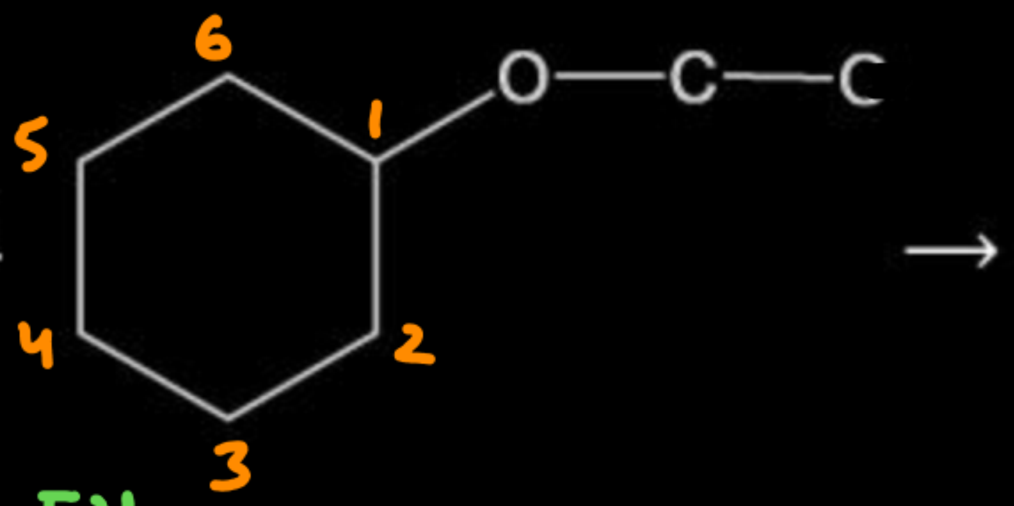
→ Smaller alkoxy carbon, Bigger alkane carbon.

Examples:

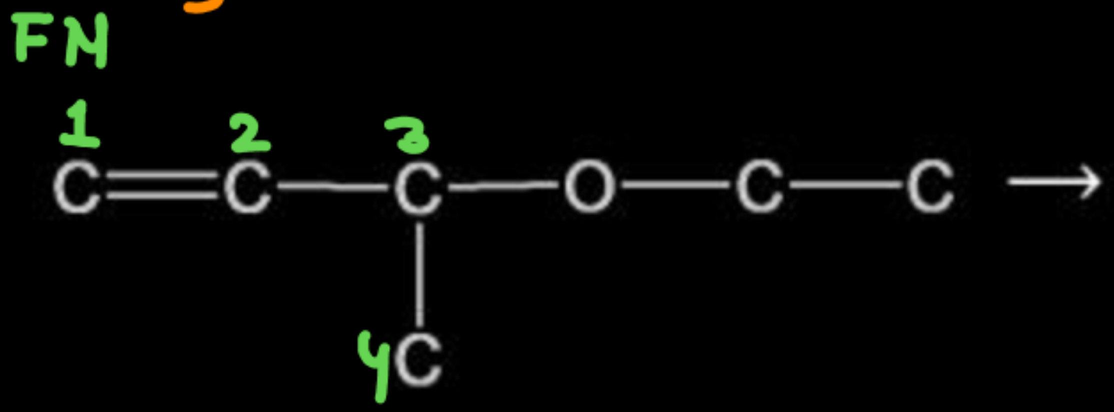
1. C—O—C—C (numbered 1, 2) → 1-methoxyethane

2. C—C—O—C—C (numbered 1, 2) → 1-ethoxyethane

3.  → 2-methoxypropane

4. 

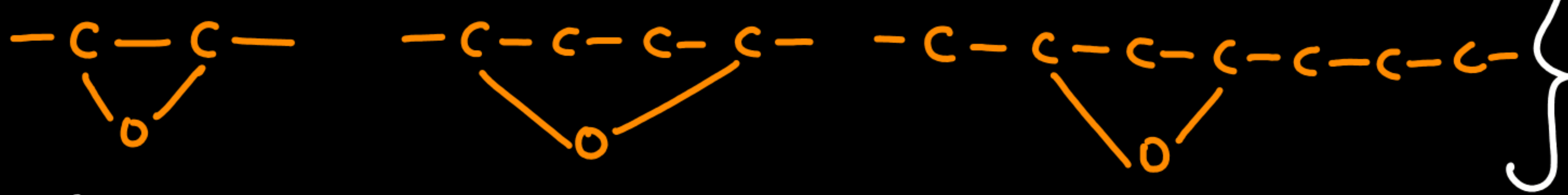
1-ethoxycyclohexane

5. 

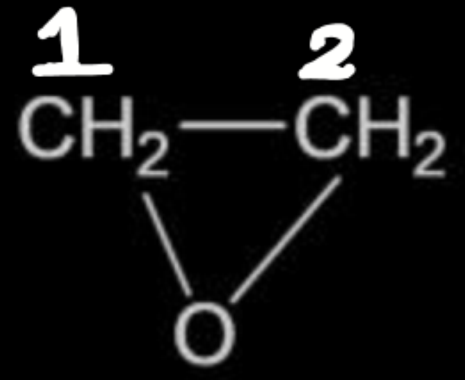
3-ethoxybut-1-ene

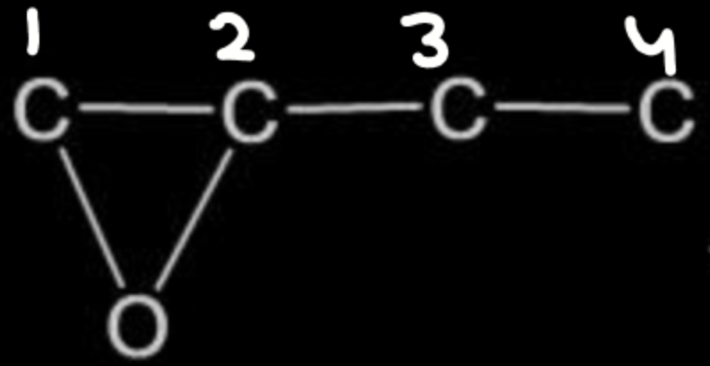
6. C-C-C-C-C-O-C=C (1 2)

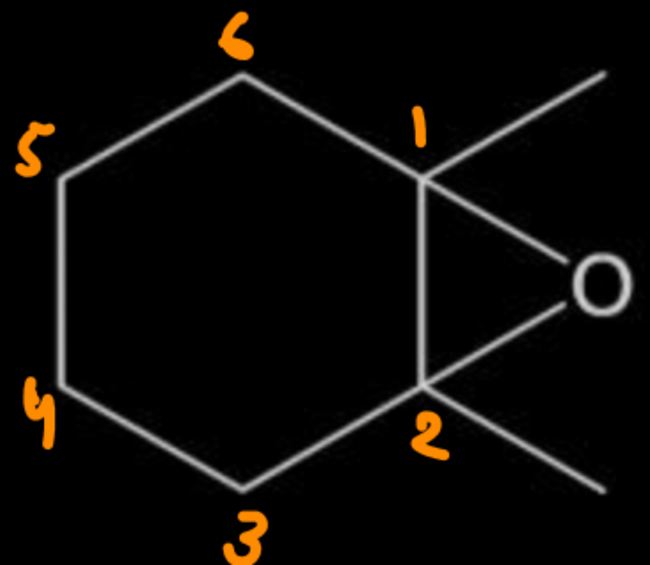
1-pentoxyeth-1-ene / Pentoxyethene



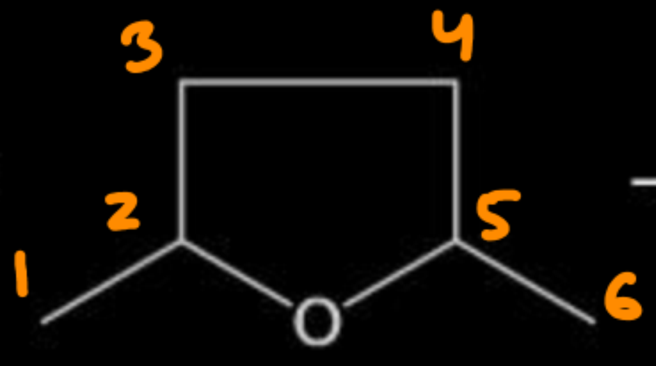
EPOXIDE → Prefix → epoxy

1.  → 1,2-epoxyethane

2.  → 1,2-epoxybutane

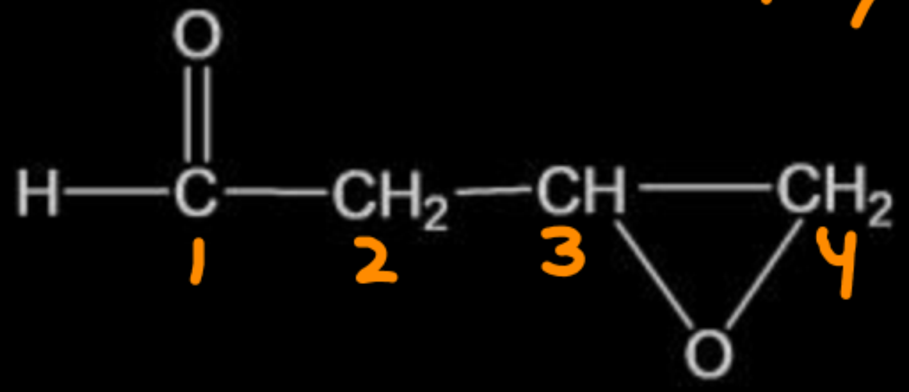
3.  →  1,2-epoxy-1,2-dimethylcyclohexane

4.



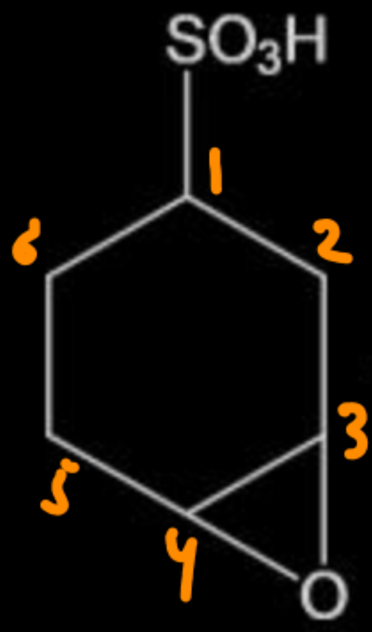
→ 2,5-epoxy hexane

5.



→ 3,4-epoxybutane-1-al

6.

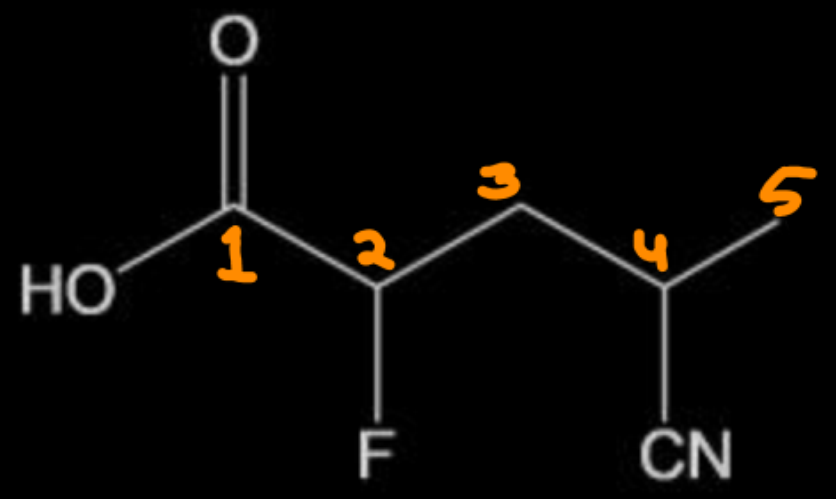


→ 3,4-epoxycyclohexane-1-sulphonicacid

Poly Functional Group

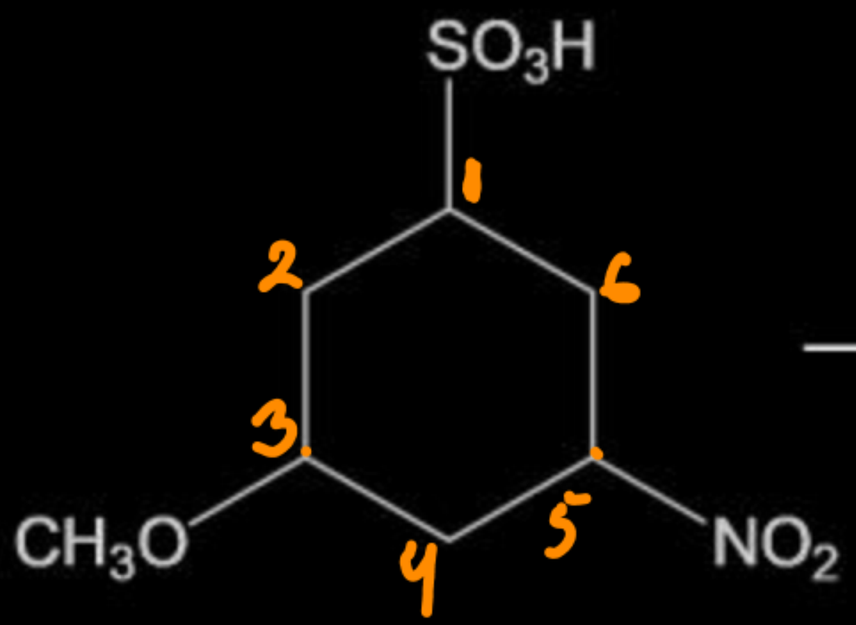
21012

Examples:

1.  →

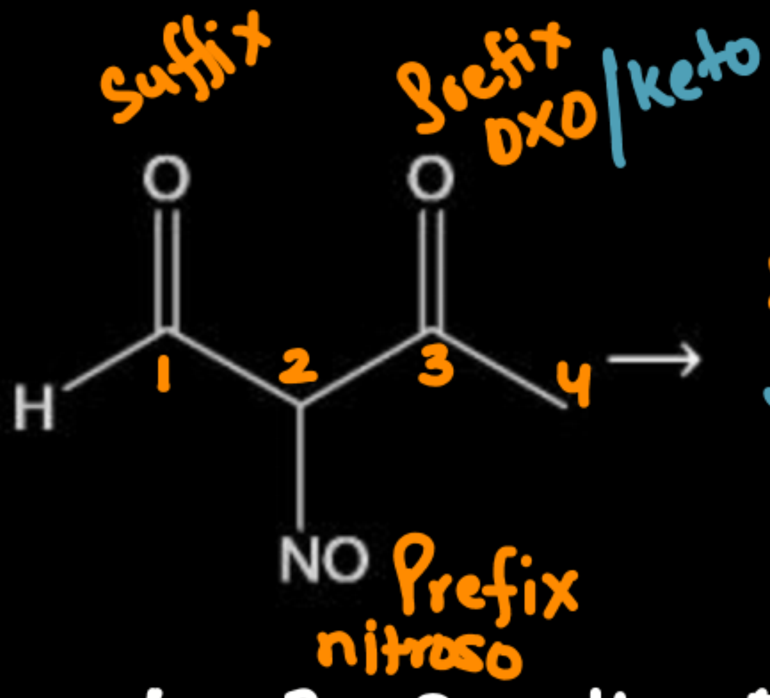
4-cyano-2-fluoropentan~~e~~-1-oicacid

21012

2.  →

3-methoxy-5-nitrocyclohexane-1-sulphonic acid

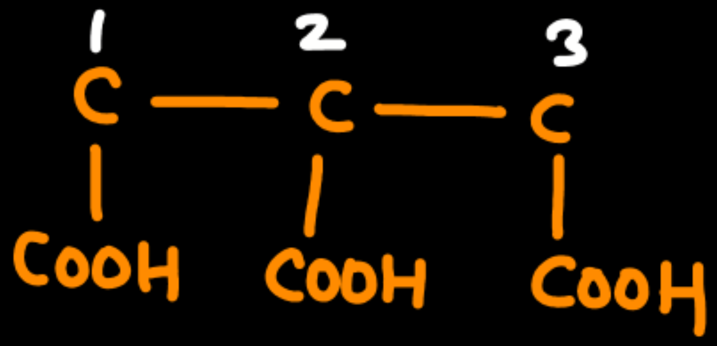
3.



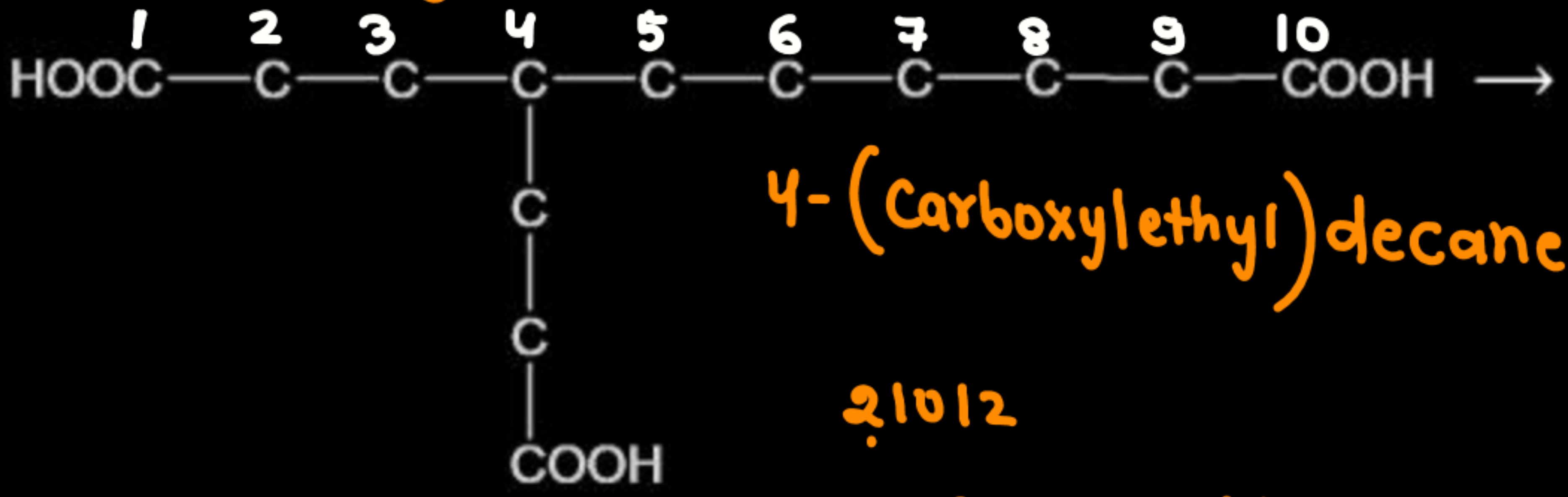
2-nitroso-3-oxobutane-1-al

3-Keto-2-nitrosobutane-1-al

2,1,0,1,2



4.

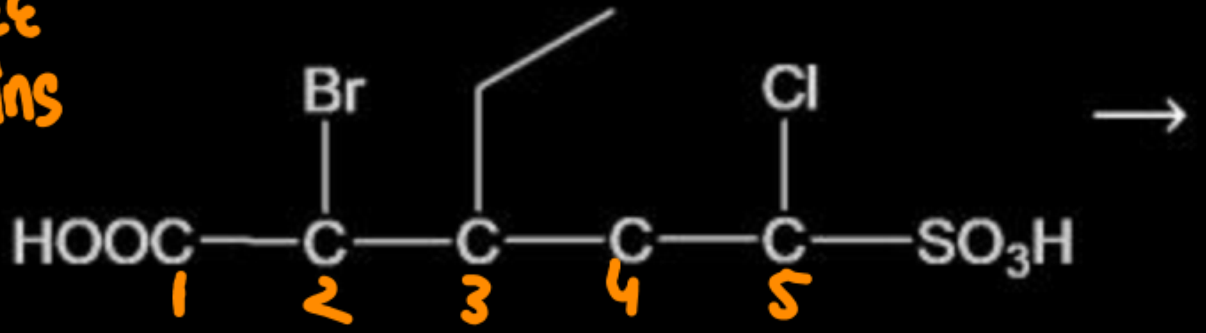


4-(Carboxylethyl)decane-1,10-dioic acid

21012

IIT-JEE Mains

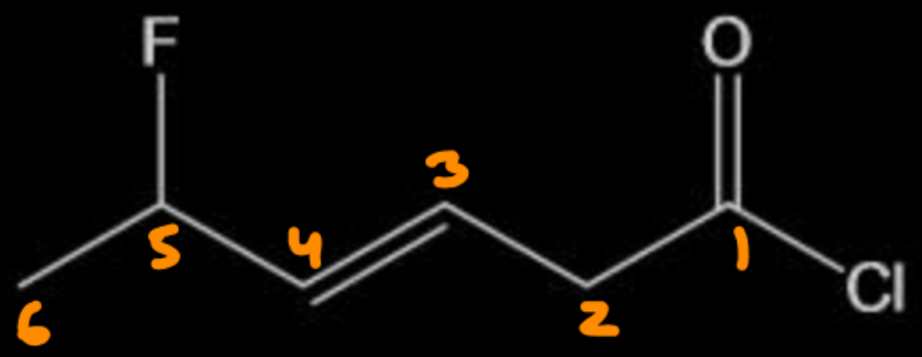
5.



2-Bromo-5-chloro-3-ethyl-5-sulphopentane-1-oicacid

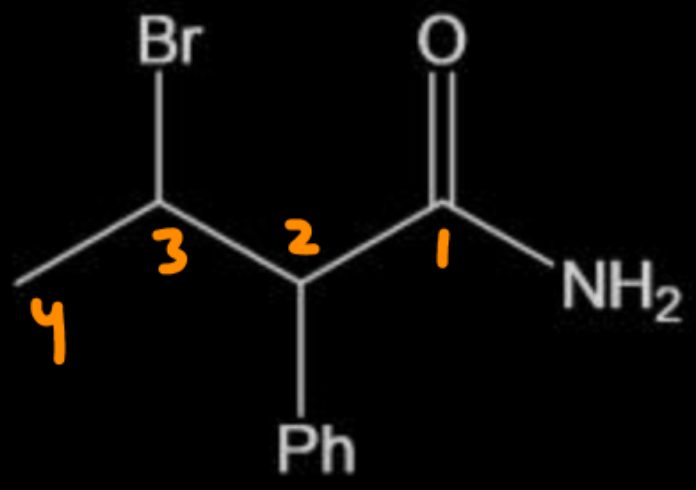
Acp Aunty mam

2 1 0 1 2

6. 

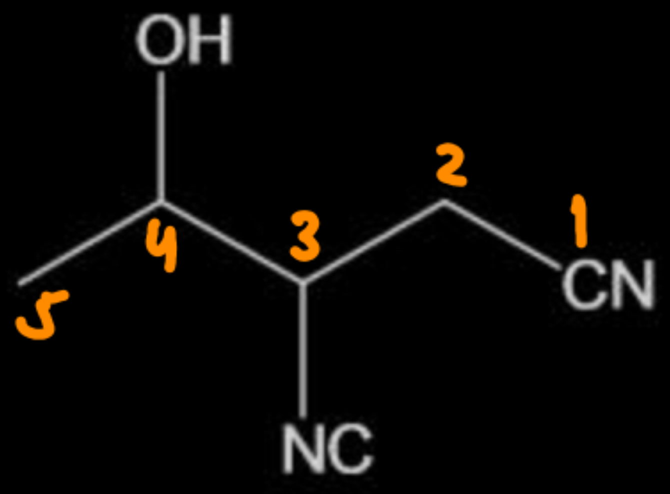
→ 5-fluorohex-3-ene-1-oylchloride

2 1 0 1 2

7. 

→ 3-Bromo-2-phenylbutane-1-amide

~~2 1 0 1 2~~

8. 

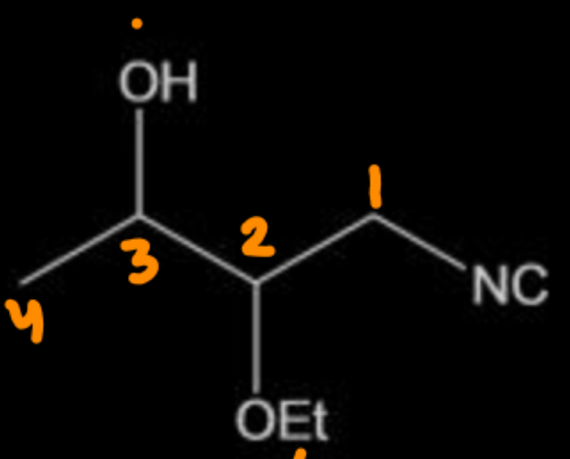
→

4-Hydroxy-3-isocyanopentane-1-nitrile

3-Carbylamino-4-hydroxypentane-1-nitrile

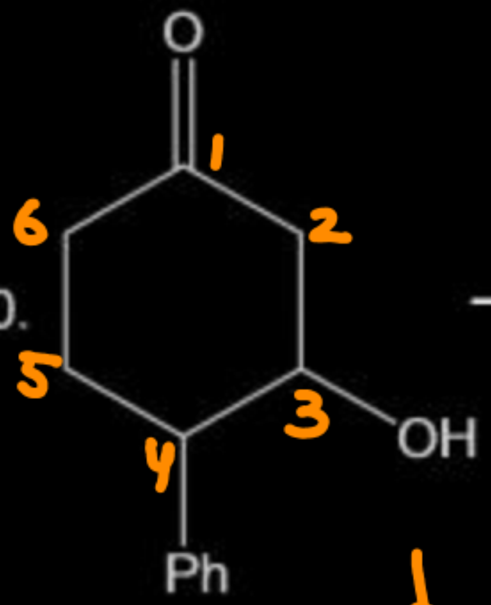
OMe → $O-CH_3$
OEt → $O-CH_2-CH_3$

21012

9. 

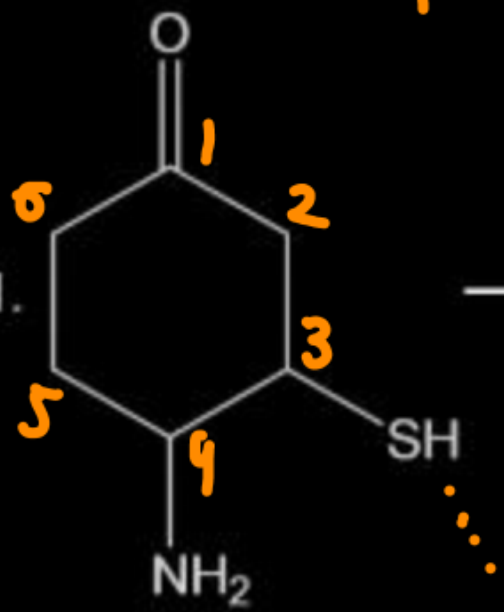
→ 2-ethoxy-3-hydroxybutane-1-isonitrile

21012

10. 

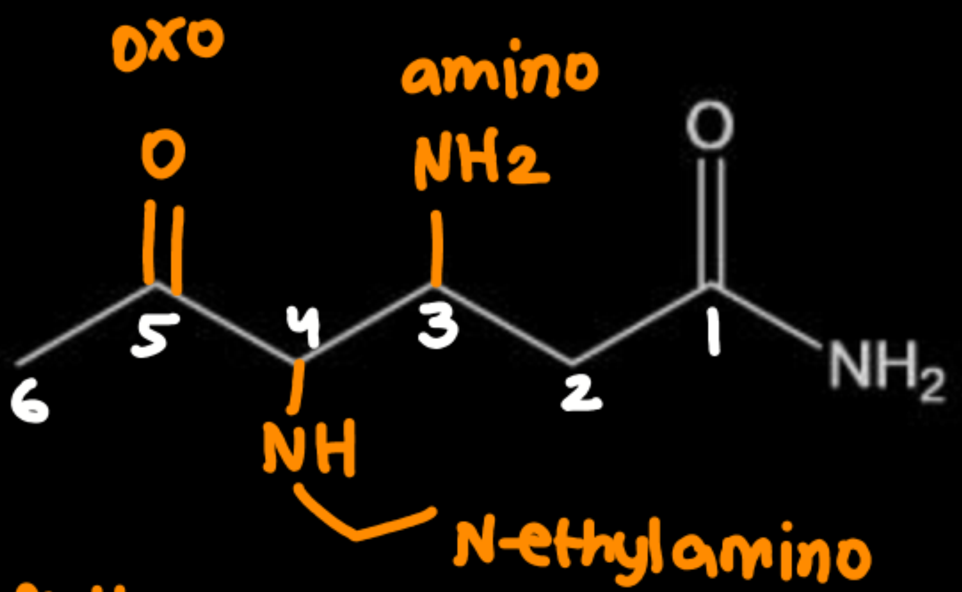
→ 3-Hydroxy-4-phenylcyclohexane-1-one

21012

11. 

→ 4-amino-3-merceptocyclohexane-1-one

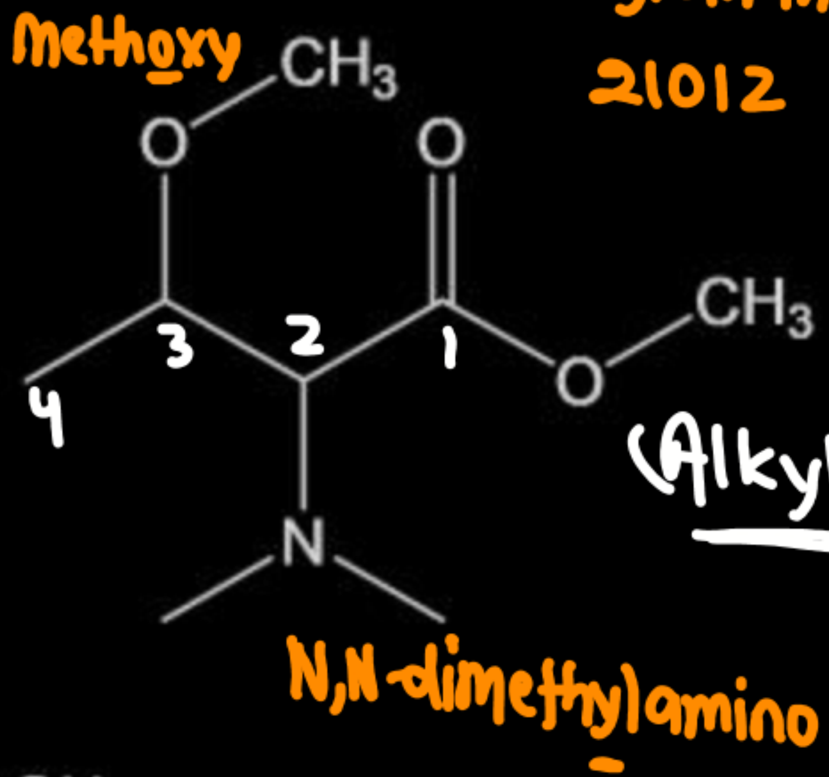
12.



→ 3-amino-4-N-ethylamino-5-oxohexan~~e~~-1-amide

21012

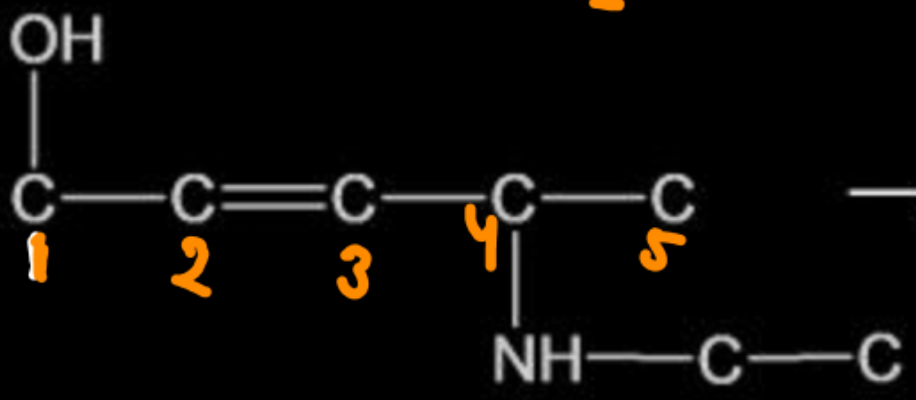
13.



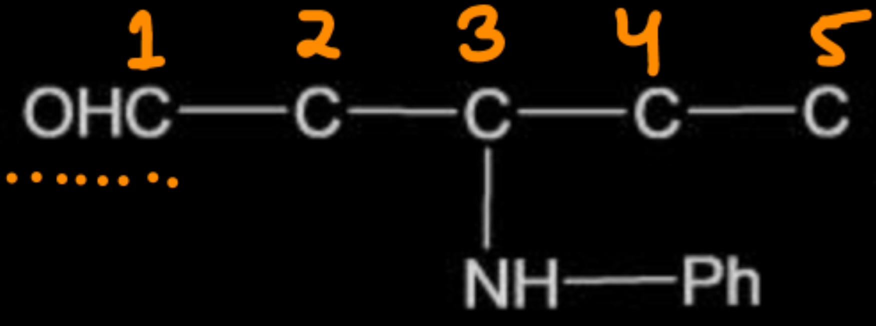
→ Methyl-3-methoxy-2-(N,N-dimethylamino)butan~~e~~-1-oate

(Alkyl Alkanoate)

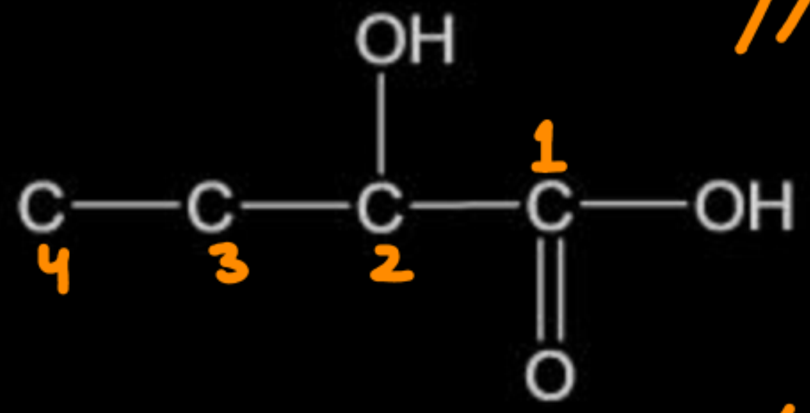
14.



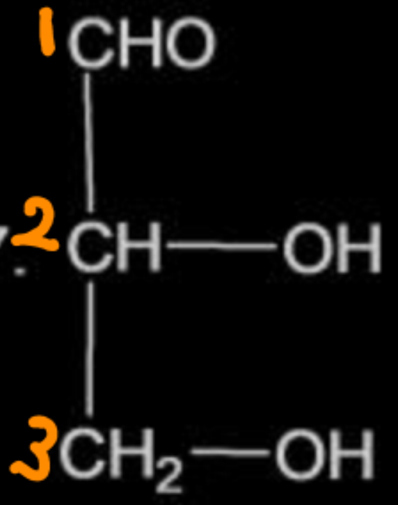
→ 4-(N-ethylamino)pent-2-en~~e~~-1-ol

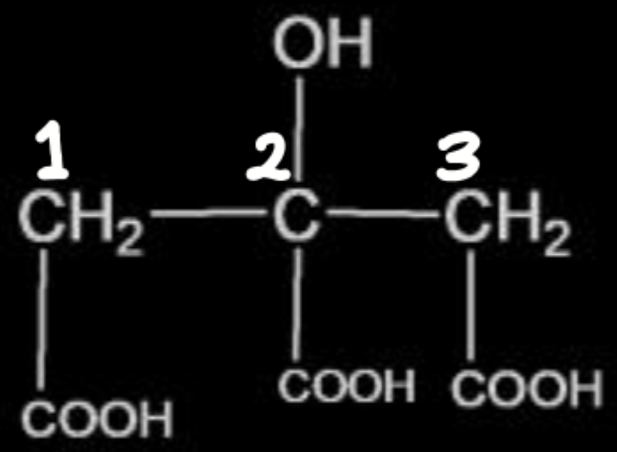
15.  → 3-(N-phenylamino)pentan~~e~~-1-al

~~3/1/0/2~~

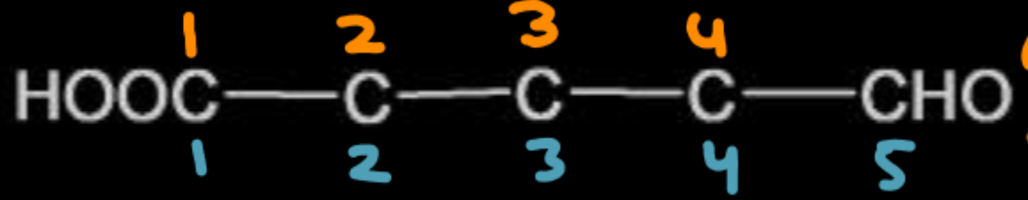
16.  → 2-Hydroxybutan~~e~~-1-oicacid

~~2/1/0/2~~

17.  → 2,3-dihydroxypropan~~e~~-1-al

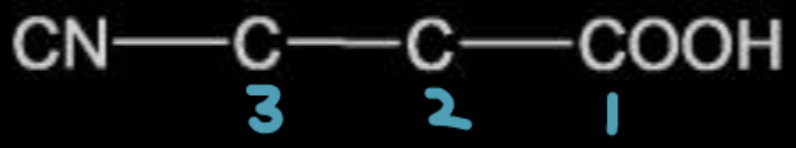
18. 

→ 2-Hydroxypropane-1,2,3-tricarboxylic acid

19. 

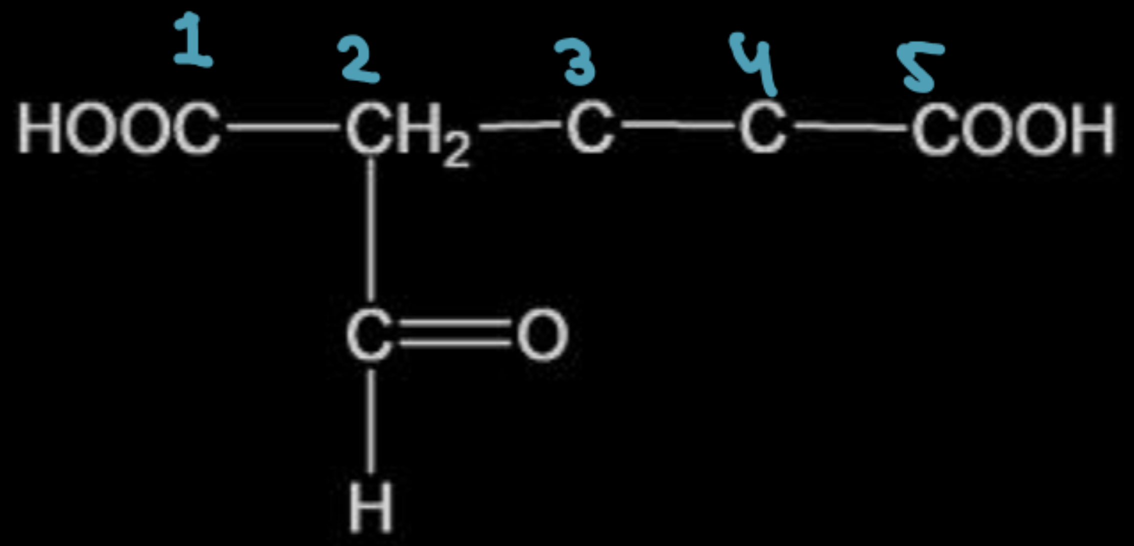
→ 4-formylbutane-1-oic acid

→ 5-oxopentane-1-oic acid

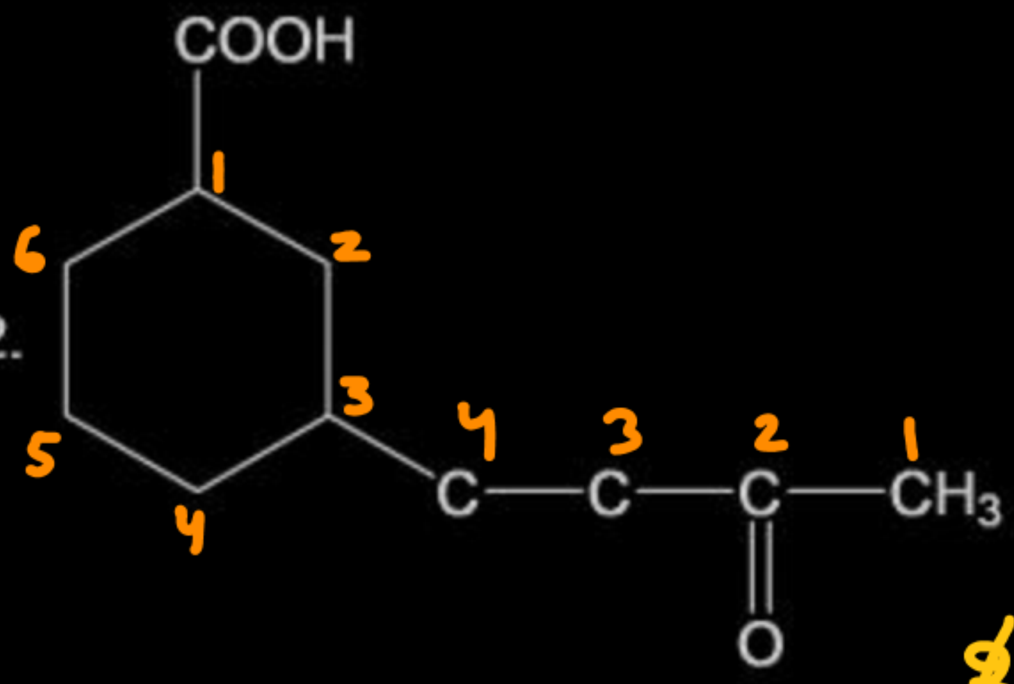
20. 

→ 3-isocyanopropane-1-oic acid

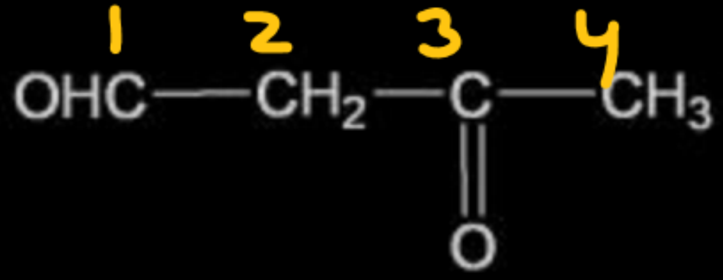
3-Carbylaminopropane-1-oic acid

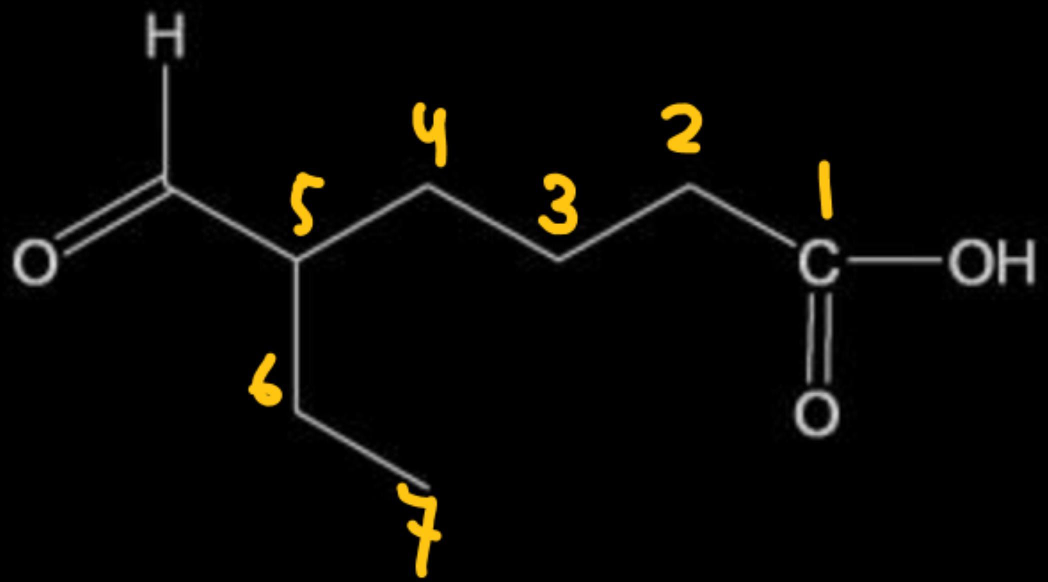
21. 

→ 2-formylpentane-1,5-dioic acid

22.  → 3-(2-oxobutyl)cyclohexane-1-carboxylic acid

8/012

23.  → 3-oxobutan~~e~~-1-al

24.  → 5-formylheptan~~e~~-1-oic acid

Chapter 1 : Basics of organic chemistry

Chapter 2 : IUPAC Nomenclature (Common naming)

* Chapter 3 : Isomerism

↳ neet → 2 Que → 8 marks

Isomerism

Iso – Same
Meros – Part } Same MF

Two or more compounds having same Molecular Formula (MF) but having diff properties.

↓

* either physical property is diff
* Or Chemical property is diff
* Or both the properties are diff.

Comp showing isomerism is called isomers.

eg # C_3H_8O → $CH_3-CH_2-CH_2-OH$
→ $CH_3-O-CH_2-CH_3$

} diff Property becoz of diff Functional Group.

Same MF, Same GF, Same EF, Same Mwt, Same Vapour density, Same DU, Same % composition of element.

Isomerism

Space → 3d → spatial

Structural isomerism or, Constitutional isomerism

IUPAC Name diff.

→ Same MF, Connectivity is diff
structure is diff

1. → Chain Isomerism / Skeletal isomer / Branch chain isomer
2. → Position Isomerism
3. → Ring chain Isomerism
4. → Functional Group Isomerism
5. → Metamer
6. → Tautomer

Stereo Isomerism

IUPAC Name Same

MF Same, Connectivity is same
but angle b/w bond in 3d is diff.
(Spatial arrangement is diff)

- Configurational Isomerism
  - Geometrical Isomerism (GI)
  - Optical Isomerism (OI)
- Conformational Isomerism

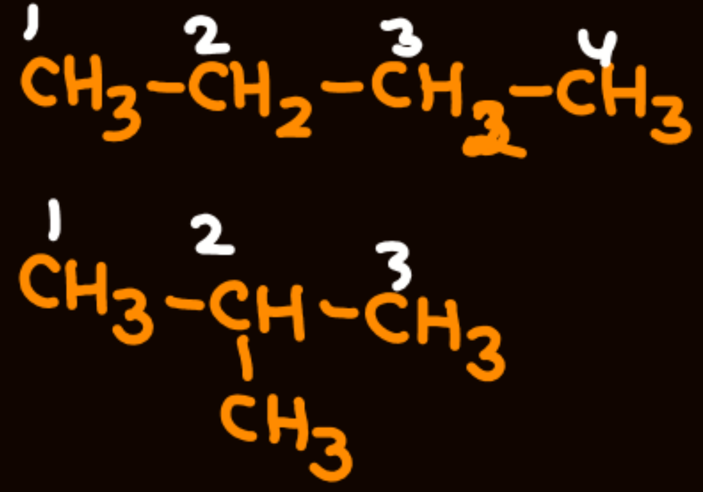
MF - Same → CI
PCC, SC] diff

Chain Isomerism

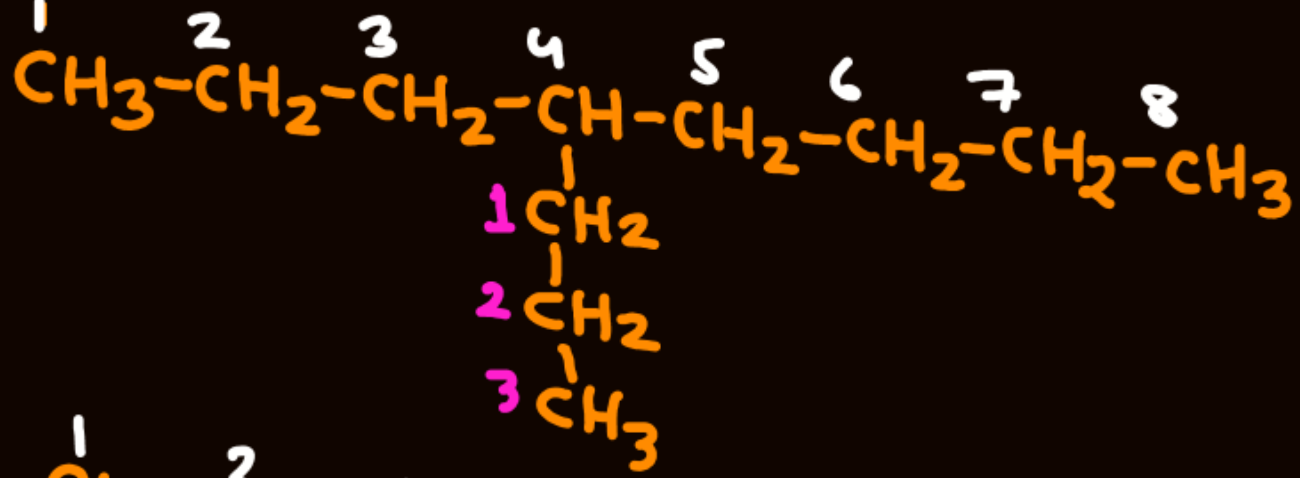
① Same MF, Same GF, Same EF, Same MWt, Same Vd, Same DU, Same % composn of element

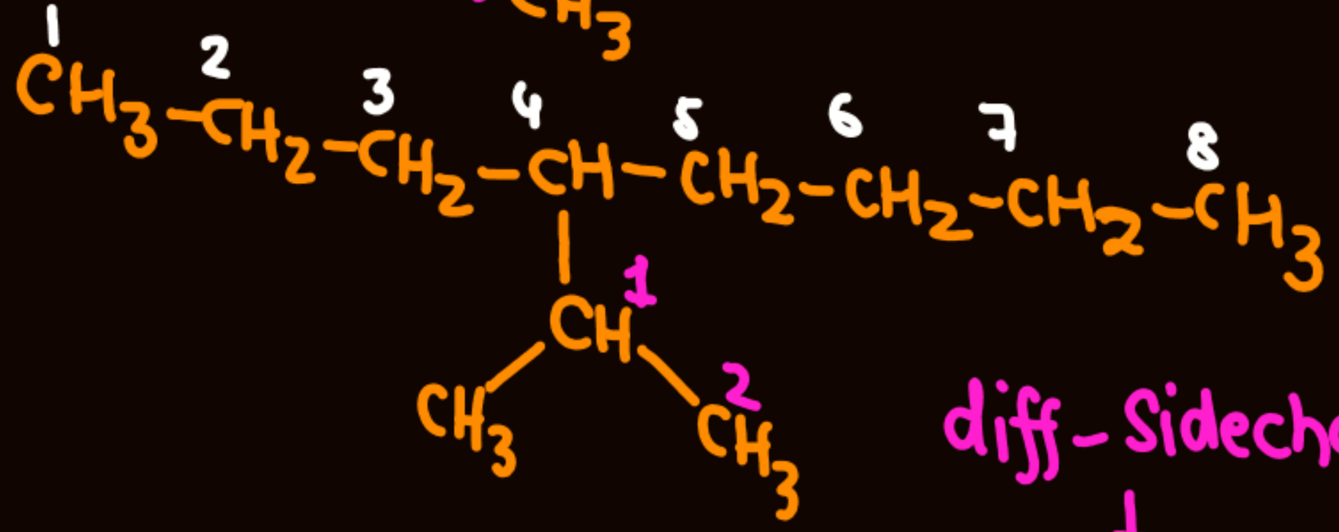
② diff property due to different parent chain (diff no of Carbon in PCC)
or, due to different Side chain (Substituent or branch)
(diff no of carbon in side chain)

eg.

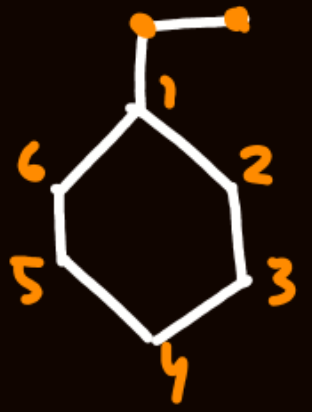


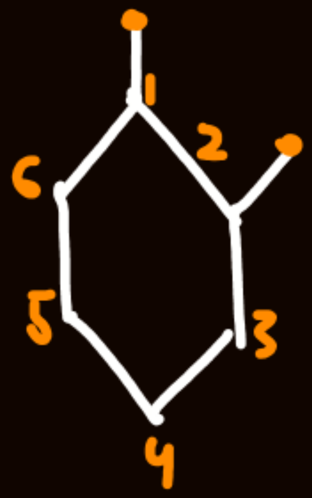
PCC → diff
↓
CI





diff - Sidechain
↓
CI





Sidechain
↓
diff
↓
CI

Position Isomerism

① Same MF, Same GF, Same EF, Same Mwt, Same Vd, Same DU, Same % composⁿ of element, Same PCC & SC

② diff property → due to change in position of same Multiple bond (=, ≡)

or → due to change in position of same Functional Group

or → due to change in position of same Sidechain (Substituent/branch)

MF - Same
FG, MB, SC
↓
Posⁿ diff

Eg

C-C-C=C

C-C=C-C

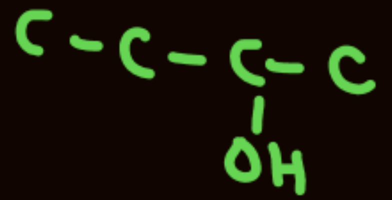
Eg

C-C-C-C≡C

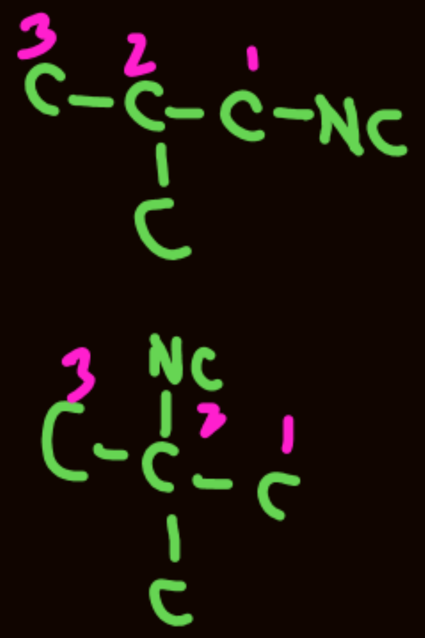
C-C-C≡C-C

Eg

C-C-C-C-OH



Eg



Eg



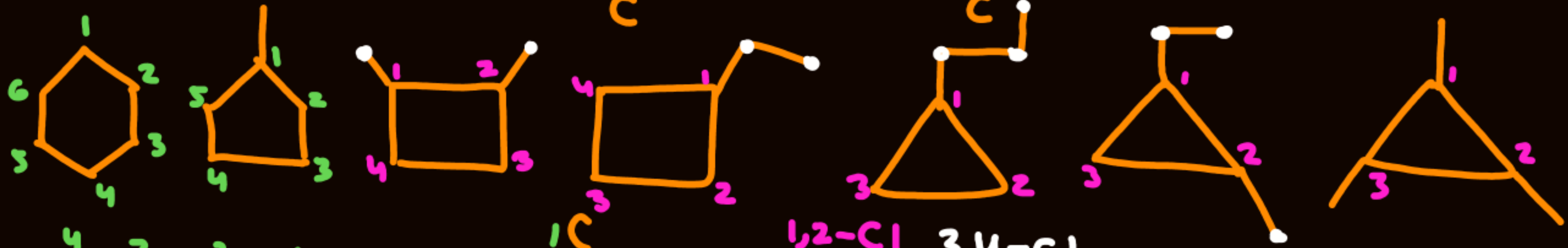
Eg



Que Find Relation -

Cl ① 

Cl ② 

③ 

Cl ④ 

1,2-Cl	3,4-Cl
1,3-Cl	3,5-Cl
1,4-Cl	3,6-Cl
1,5-Cl	3,7-Cl
1,6-Cl	4,5-Cl
1,7-Cl	4,6-Cl
2,3-Cl	4,7-Cl
2,4-Cl	5,6-Cl
2,5-Cl	5,7-Cl
2,6-Cl	6,7-Cl
2,7-Cl	

⑤ 

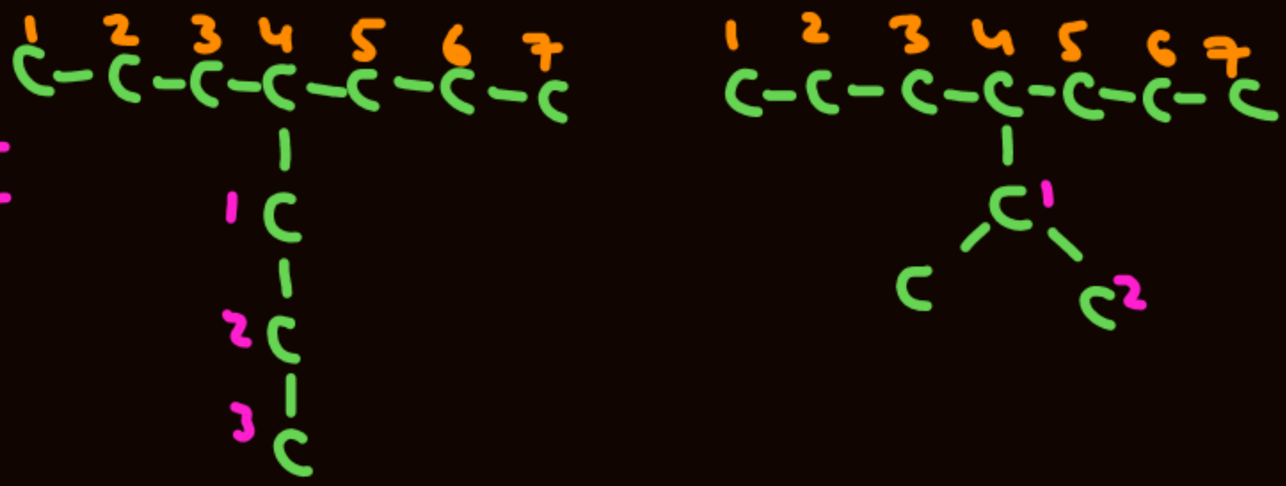
✓ identical
✓ Same
✓ Homomer

⑥ 

identical
Homomer

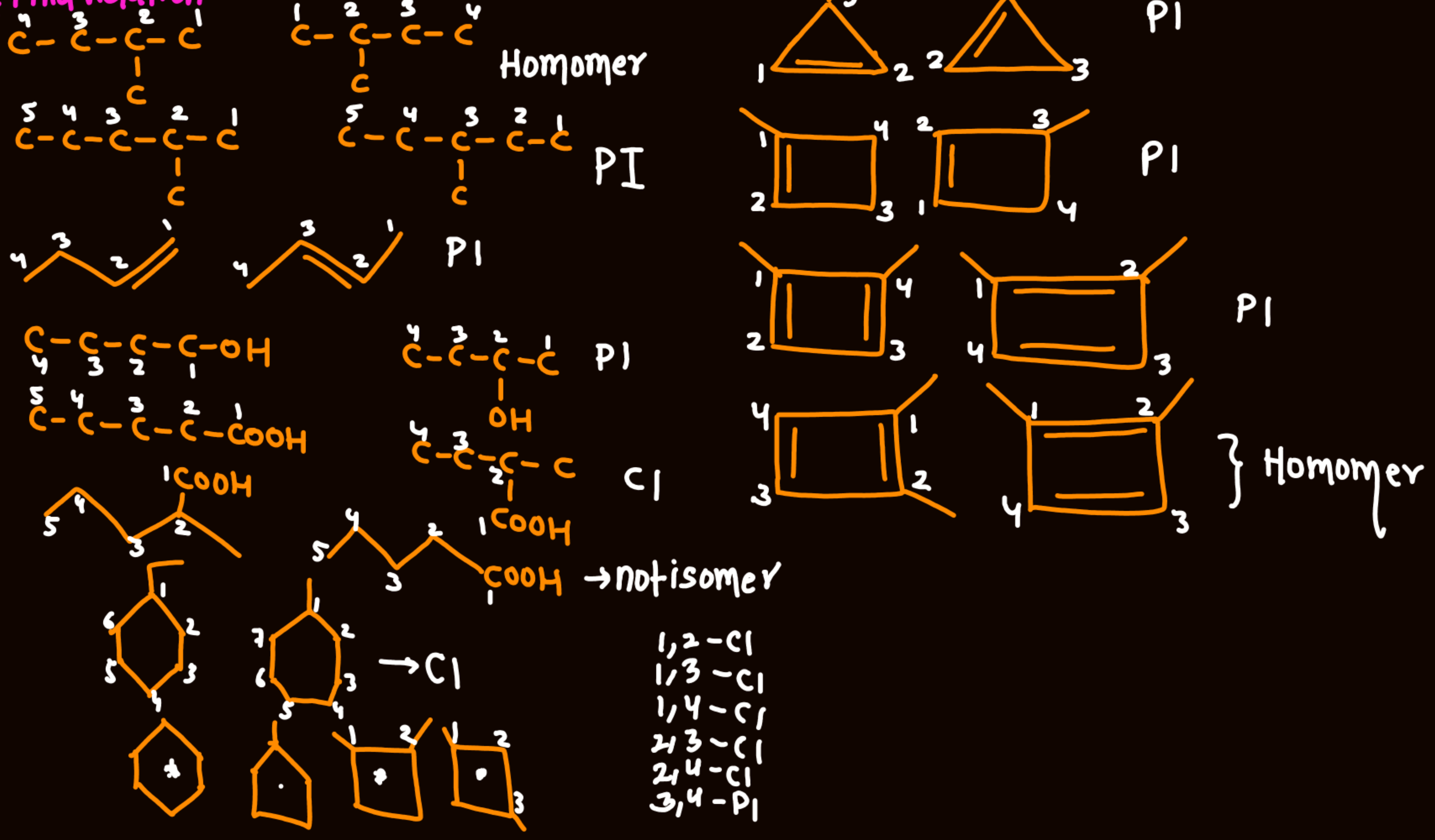
CI ⑦ 

CI ⑧ 

⑨ CI 

note → Identical comp (Homer) have Same IUPAC name.

Que Find Relation-



note → All RCI are also FI

Ring Chain Isomerism

RCI → ✓ MF Same, ✓ DU Same, { one is Ring & other is openchain }

- Same MF, GF, EF, MWt, Vd, % composition, DU
- diff property because of diff Connectivity → one Comp is open chain → other Comp is Ring
- MIN DU ≥ 1.

Eg →



DU=1



DU=1

MF - same
DU - Same
diff - Connectivity
} RCI





RCI



DU=2



DU=2

RCI



C–C≡C RCI



DU=1

C–C≡C–C–C
DU=2
} not isomer



DU=1

C–C=C–C–C–C
DU=1
} RCI

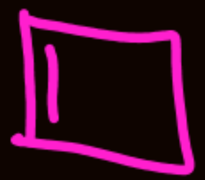
2 butyne & cyclobutane } not isomer

C–C≡C–C



2 butyne & cyclobutene } RCI

C–C≡C–C



Functional Group Isomerism

- Same MF, GF, EF, MWt, Vd, DU, % compsn
- diff property due to diff FG

MF - same
DU - same
FG - diff
} FI

Case1: alcohol & ether

CH_3-CH_2-OH

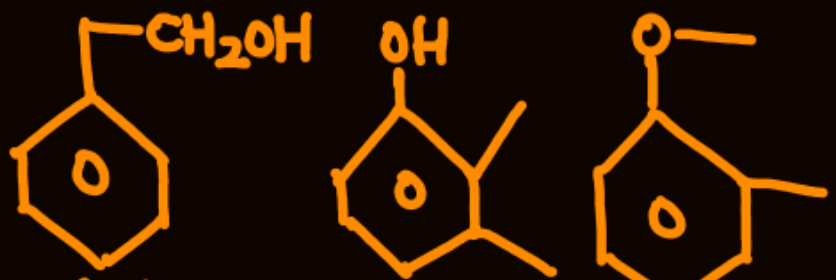
CH_3-O-CH_3

Case2: thioalcohol & thioether

CH_3-CH_2-SH

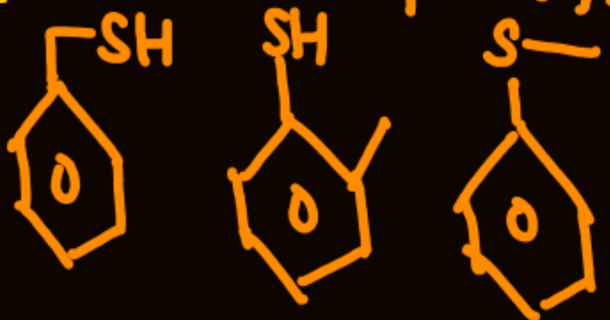
CH_3-S-CH_3

Case3: Alcohol, Phenol, Ether



alcohol Phenol ether

Case4: Thioalcohol, Thiophenol, Thioether



Case5: nitro and nitrite

$CH_3-CH_2-N(=O)\rightarrow O$

$CH_3-CH_2-O-N=O$

Case6: Carboxylic acid & Ester

$CH_3-CH_2-C(=O)-OH$

$CH_3-C(=O)-O-CH_3$

Case7: cyanide & isocyanide

$CH_3-CH_2-C\equiv N$

$CH_3-CH_2-N\equiv C$

Case8: alkyne & diene

$C-C\equiv C-C$

$C=C-C=C$

Case9: 1° amine, 2° amine, 3° amine

$CH_3-CH_2-CH_2-NH_2$

$CH_3-CH_2-NH-CH_3$

$CH_3-N(CH_3)-CH_3$

Case10: 1° amide, 2° amide, 3° amide

$CH_3-CH_2-CH_2-C(=O)-NH_2$

$CH_3-CH_2-C(=O)-NH-CH_3$

$CH_3-C(=O)-N(CH_3)-CH_3$

Case11: aldehyde & ketone

$CH_3-CH_2-C(=O)-H$

$CH_3-C(=O)-CH_3$

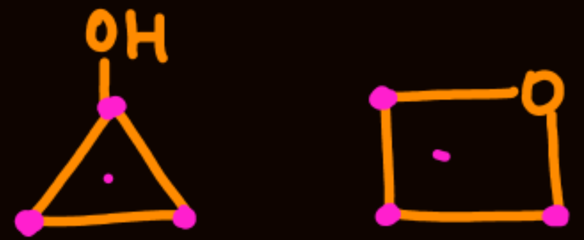
Case12: amide & oxime

$CH_3-C(=O)-NH_2$

$CH_3-C=N-OH$

Que Find Reln

① $CH_3-CH_2-C(=O)-H$ $CH_3-C(=O)-CH_3$ FI

②

FI

1,2-FI
1,3-FI
2,3-FI

C-C-C-C(=O)-OH ① C-C(=O)-O-C-C ② C(OH)-C-C-C(=O)-H ③



RCl / FI
answer

C-C≡C-C C=C-C=C } FI

1,2-FI
1,3-FI
2,3-FI

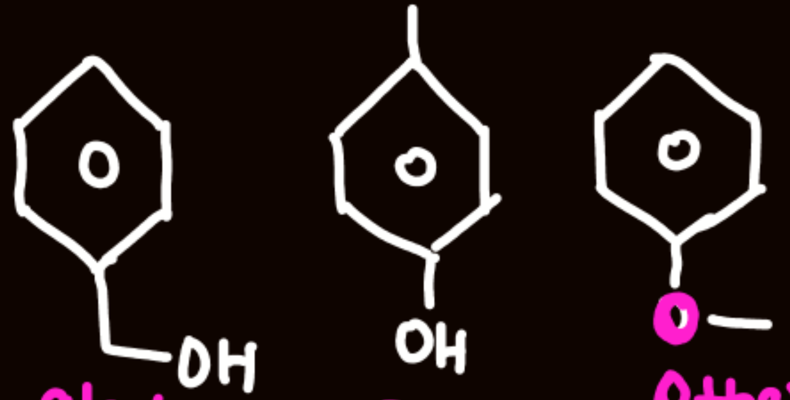
C-C-NO_2 C-C-O-N=O C(OH)-C-N=O

C-C-C(=O)-NH_2 ① amide C-C-C=N-OH ② oxime C-C(=O)-NH-C ③

1,2-FI
1,3-FI
2,3-FI

1° 2° 3° amine → 3 diff FG
1° 2° 3° amide → 3 diff FG

Q
C-C-C-C≡N
C-C-C-N≡C
FI

Q

alcohol phenol ether } FI

note → In case of more than one isomer Follow priority Rule

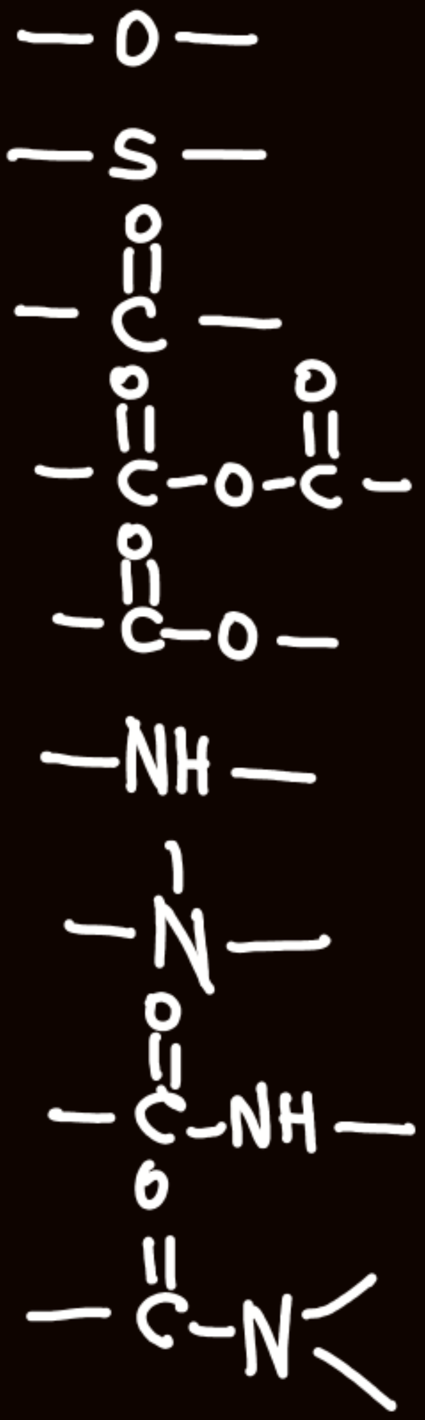
RCl — R. → Rohit
Tautomer T → Tanya
FI — F. → Fiy
Metamer M → Mile
CI — C → chemistry
PI — P → padhne

Metamer

↓ Middle

(PVFG)

Polyvalent Functional Group :-



1. Same MF, GF, EF, MWt, Vd, % compsⁿ, DU, Same PVFG
2. diff property due to diff Carbon on both side of PVFG.

NOTE → If num of Carbon on both side of PVFG is diff then comp is metamer

→ If num of Carbon on only one side of PVFG is diff then compound is metamer as well as it shows CI/PI .

Q C–O–C–C–C C–C–O–C–C Metamer

Q C–O–C–C–C C–C–C–O–C Homomer

Q C–O–C–C–C C–O–C(–C)–C Metamer ← Ans; PI

Q



Homomer

Q

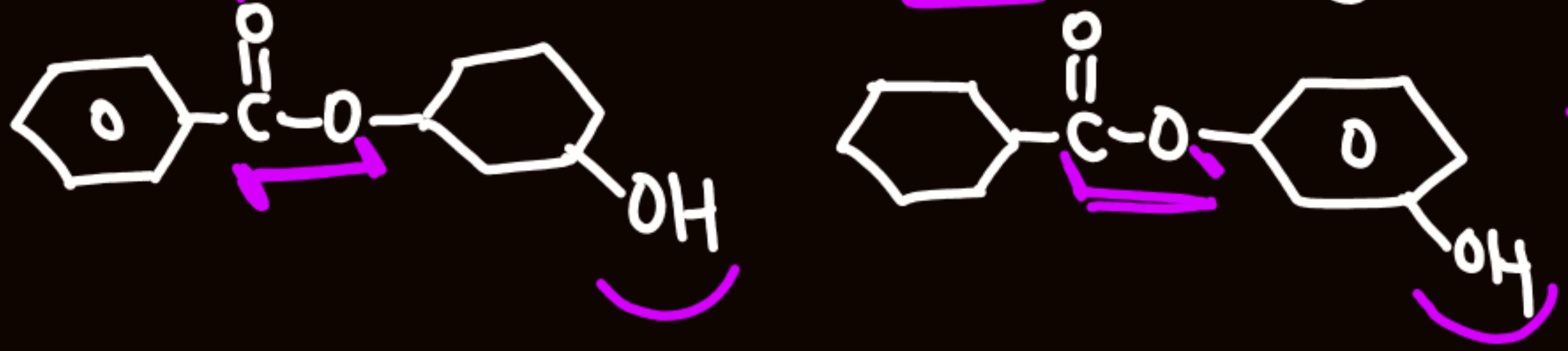


Metamer

Q CH_3–C(=O)–O–H H–C(=O)–O–CH_3 FI

Q CH_3–C(=O)–O–CH_3 H–C(=O)–O–CH_2–CH_3 Metamer

Q



metamer

FI ← Ans

Q Me–O–C(=O)–Me CH_3–O–C(=O)–CH_3

Et–O–CH=O CH_3–CH_2–O–C(=O)–H Metamer

Q CH_3–C(=O)–CH_2–CH_2–CH_3

CH_3–CH_2–C(=O)–CH_2–CH_3 Metamer

Q CH_3–C(=O)–CH_2–CH_2–CH_3

CH_3–C(=O)–CH(CH_3)–CH_3 Metamer CI

Geometrical Isomerism

Que Find min number of carbon to show chain isomerism in —

PCC → no of carbon is diff.
SC → no of carbon is diff.

① Alkane

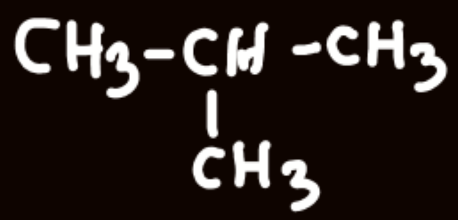
↙ 4carbon

CH_4 ✓

CH_3-CH_3 ✓

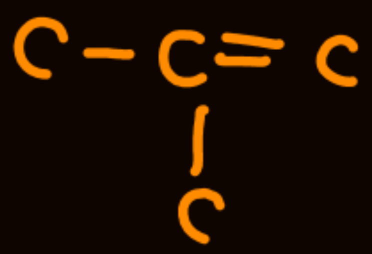
$CH_3-CH_2-CH_3$ ✓

$CH_3-CH_2-CH_2-CH_3$



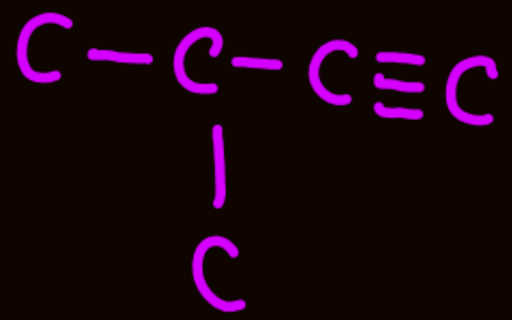
② Alkene

↙ 4 carbon



③ Alkyne

↙ 5carbon



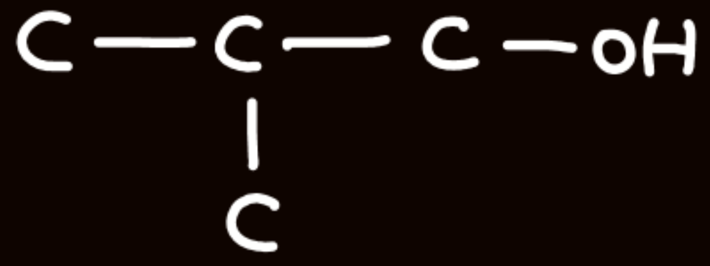
Short trick

chain isomerism
↓
Min Carbon
↓
Branch → 4 carbon

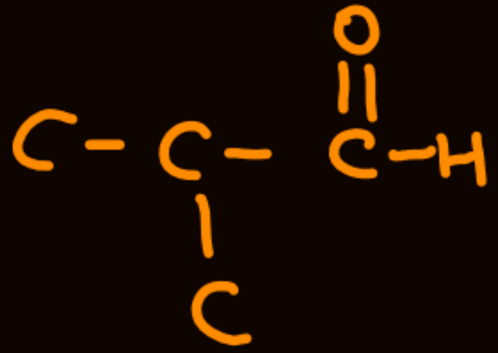


Que Find min Carbon required to Show chain Isomerism in.

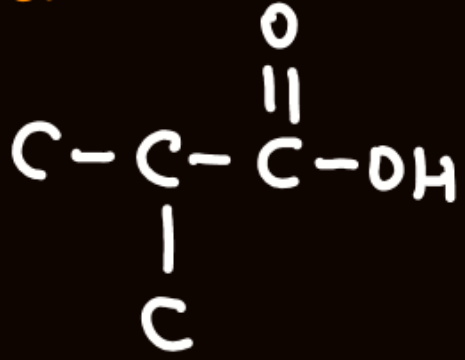
① alcohol → 4c



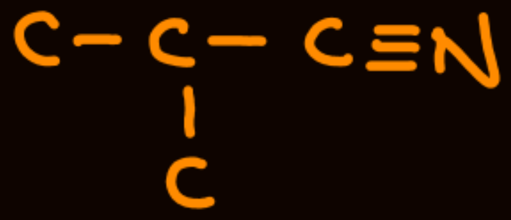
⑤ aldehyde → 4c



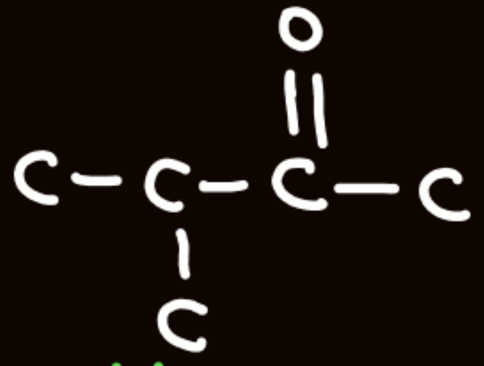
⑥ Carboxylic acid → 4c



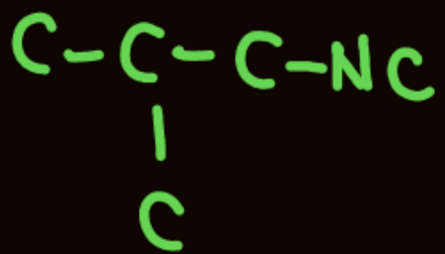
⑦ cyanide → 4c



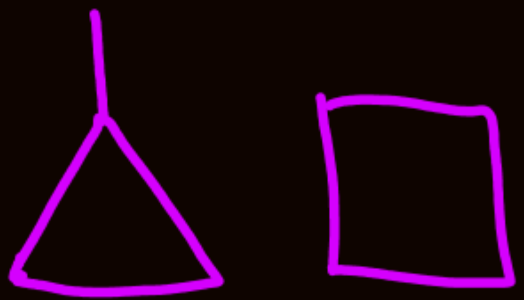
⑧ Ketone → 5c



⑨ isocyanide → generally PI → 5c



⑩ cycloalkane → 4c



Que Find min num of Carbon to show position isomer – ⟶ MB, FG, SC → Position change (SC)

alkene, alkyne, FG not containing Carbon, ketone

alkene 4C

C=C

C=C–C

C=C–C–C
C–C=C–C] PI

alkyne 4C

C≡C

C–C≡C

C≡C–C–C
C–C≡C–C } PI

Ketone 5C

C–C(=O)–C

C–C(=O)–C–C (1, 2, 3, 4)

C–C(=O)–C–C–C
C–C–C(=O)–C–C } PI

isocyanide 4C

C–NC

C–C–NC

C–C–C–NC

C–C(NC)–C

alcohol 3

C–OH

C–C–OH

PI { C–C–C–OH
C–C(OH)–C

alkane, FG containing Carbon except Ketone

alkane → 6C

CH_4

CH_3-CH_3

$CH_3-CH_2-CH_3$

$CH_3-CH_2-CH_2-CH_3$

C–C(C)–C

C–C–C–C–C

C–C(C)–C–C

C–C–C–C–C–C

C–C(C)–C–C–C
C–C–C(C)–C–C } PI

, **aldehyde*** (5C)

C–C(C)–C–CHO

C–C(CHO)(C)–C

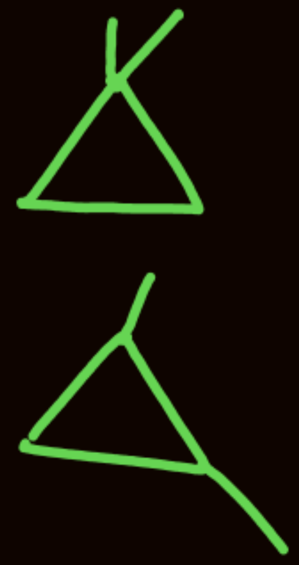
• **Carboxylic acid*** (5C)

C–C(C)–C–COOH

C–C(COOH)(C)–C

(There is change)

cycloalkane



Calculate Total num of Isomers

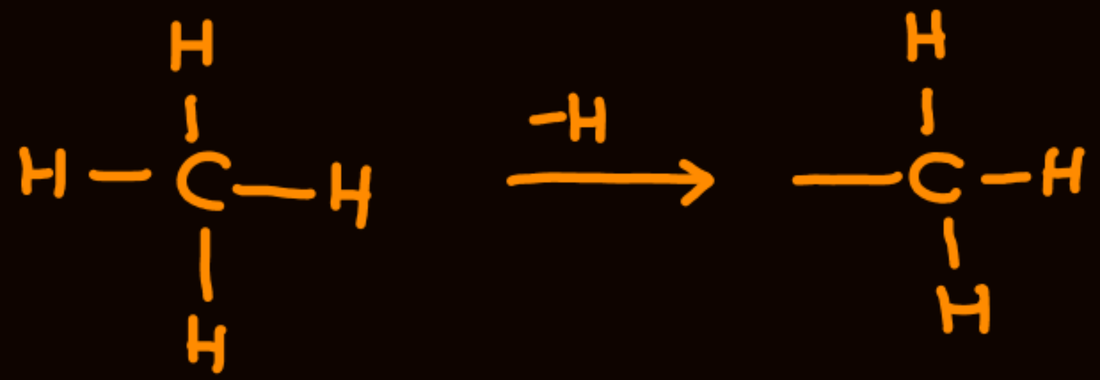
Calculation of Monovalent Radical (MR)

Monovalent → Removal of one Hydrogen

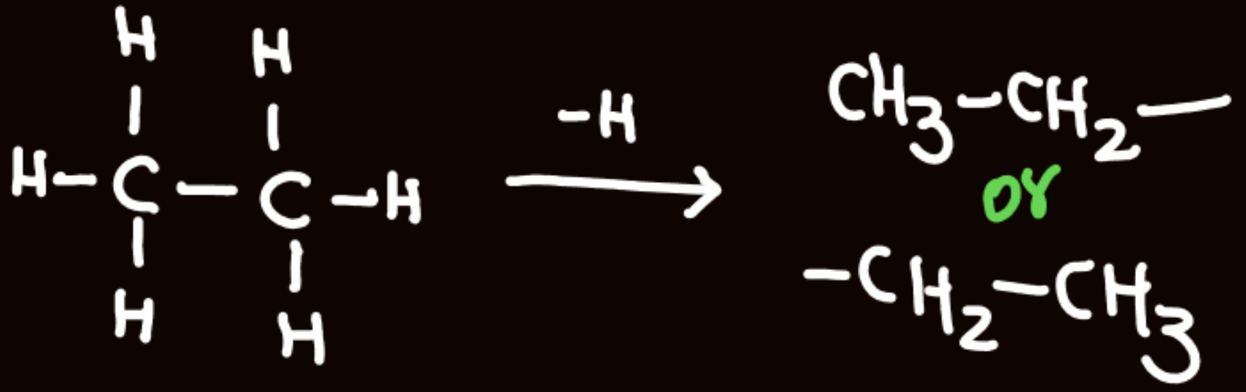
Radical → Comp formed after removal of Hydrogen

Monovalent Radical (MR) → Comp formed after removal of one Hydrogen is MR.

<u>Que</u> Cal total num of monovalent Radical in CH_4 → 1 MR



<u>Que</u> Cal total num of monovalent Radical in C_2H_6



→ 1 MR

Que Cal MR in C_3H_8

$CH_3-CH_2-CH_3$ (2°, 1°) $\longrightarrow$

$CH_3-CH_2-CH_2-$ npropyl

$CH_3-\underset{|}{C}H-CH_3$ isopropyl

} 2MR

Que Cal MR in C_4H_{10} → **4 MR**

$CH_3-CH_2-CH_2-CH_3$ nbutane (2°, 1°) →

C–C–C–C– nbutyl

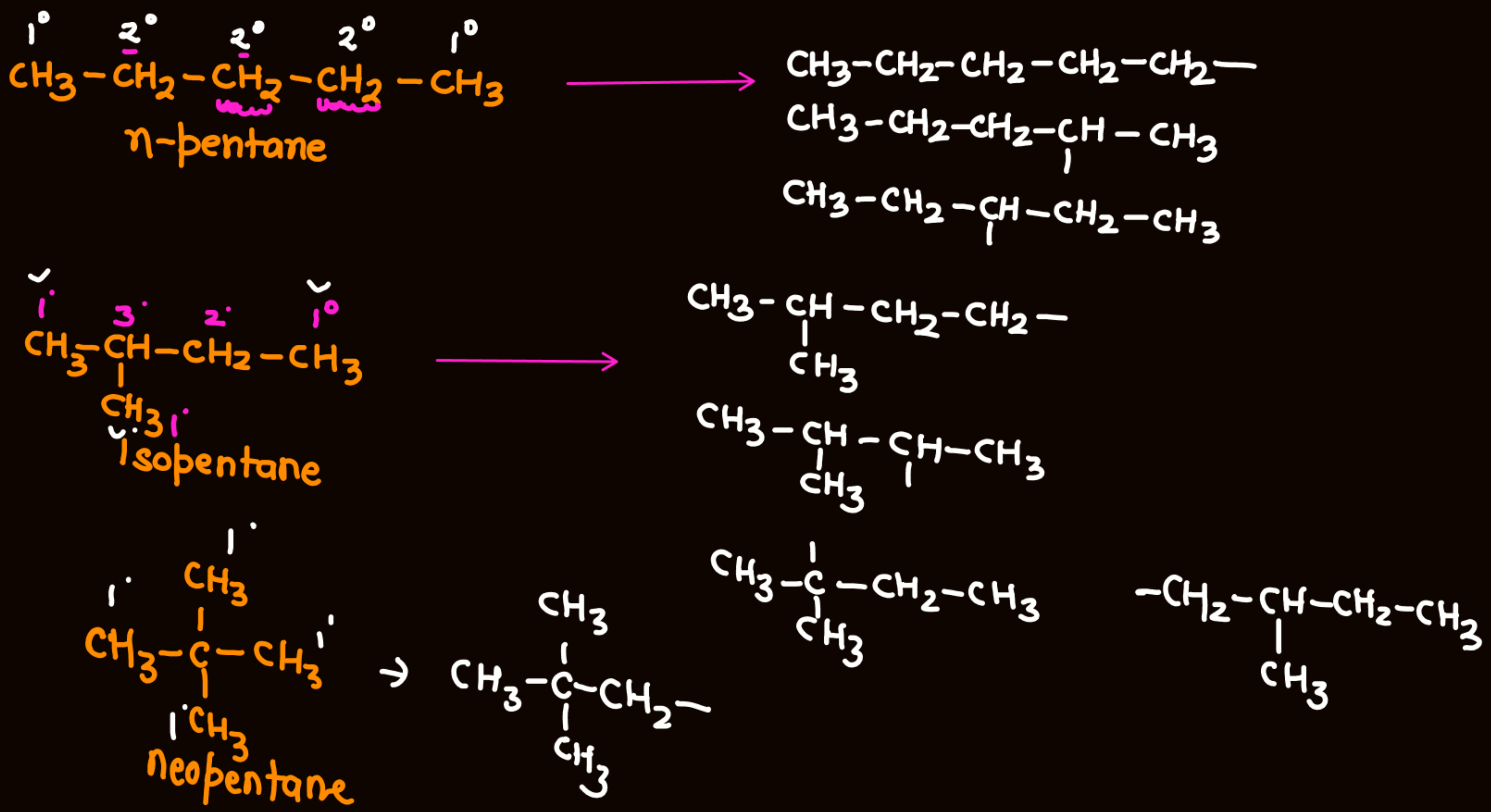
C–C–C(|)–C Secbutyl

$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_3$ (1°, 3°, 1°) isobutane

C–C(–C)–C– isobutyl

C–C(–C)(|)–C tertbutyl

Q C_5H_{12} → MR ?? → 8MR



Monovalent Radical Table

MR-Table

$CH_4 \longrightarrow$	1
$C_2H_6 \longrightarrow$	1
$C_3H_8 \longrightarrow$	2
$C_4H_{10} \longrightarrow$	4
$C_5H_{12} \longrightarrow$	8
* $C_6H_{14} \longrightarrow$	17

Calculation of Total Structural Isomer (TSI)

Que Cal TSI in CH_4.

Step 1 → DU $= (C+1) - \left(\frac{H+X-N}{2}\right)$

$= 2 - \left(\frac{4+0-0}{2}\right)$

$= 0$

CH_4

→ donot show structural isomerism.

Que2 Cal TSI in C_2H_6

DU $= 3 - \left(\frac{6}{6}\right) = 0$ → openchain & Singlebond

CH_3-CH_3

→ donot show structural isomer.

Que Cal TSI in C_3H_8

DU = 0 openchain & Singlebond

$CH_3-CH_2-CH_3$

→ donot show structural isomerism.

Que Cal TSI in C_4H_{10}.

DU = 0 openchain & Singlebond

$CH_3-CH_2-CH_2-CH_3$

$CH_3-CH(CH_3)-CH_3$

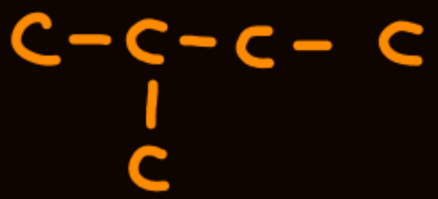
} 2 TSI

Que Cal TSI in C_5H_{12} → 3 TSI

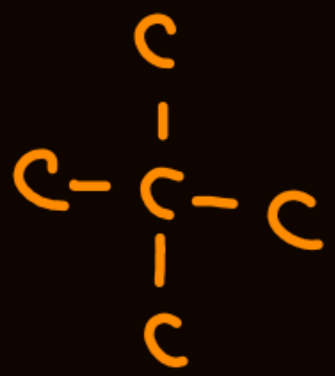
DU = 0 openchain & Single bond



npentane



isopentane

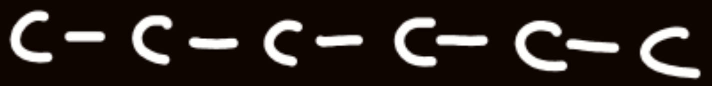


neopentane

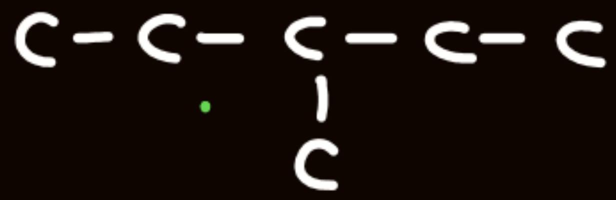
C_6H_{14} → 5 TSI

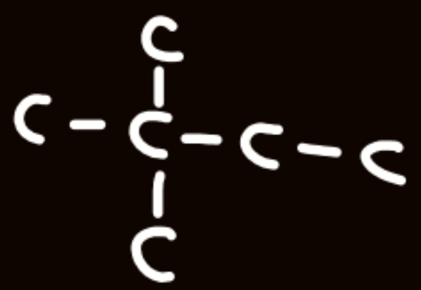
DU = 0

openchain & Single bond









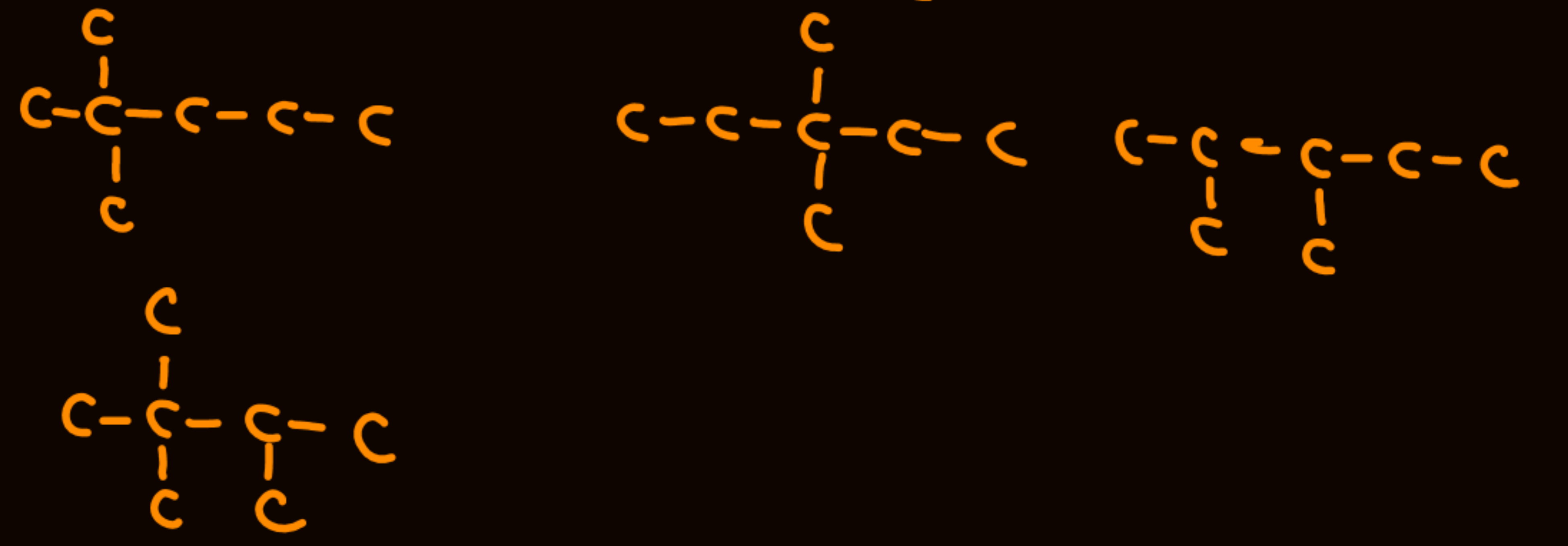


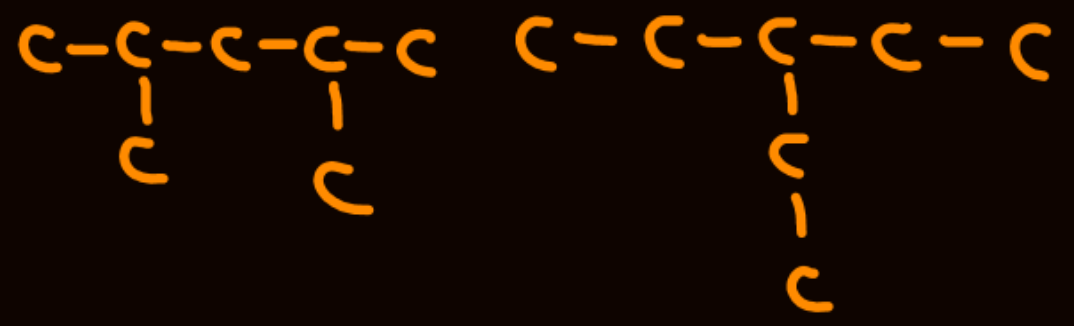
Q C_7H_{16} TSI ?? ⟶ 9 TSI

DU = 0

open chain & Singlebond







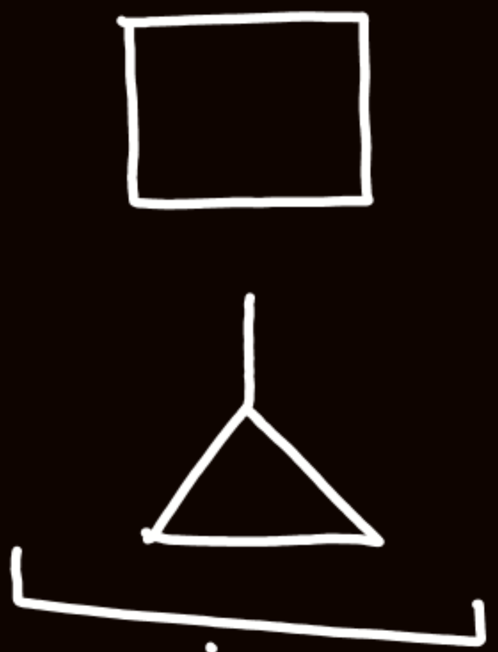
Alkane ↳

comp	TSI
CH_4	0
C_2H_6	0
C_3H_8	0
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9

Que Cal TSI in C_4H_8

DU = 1 → cyclic → 1 Ring
↳ acyclic → 1 double bond

cyclic



2 isomer

acyclic

C=C–C–C

C–C=C–C



3 Isomer

Cyclic isomer — 2

acyclic " → 3

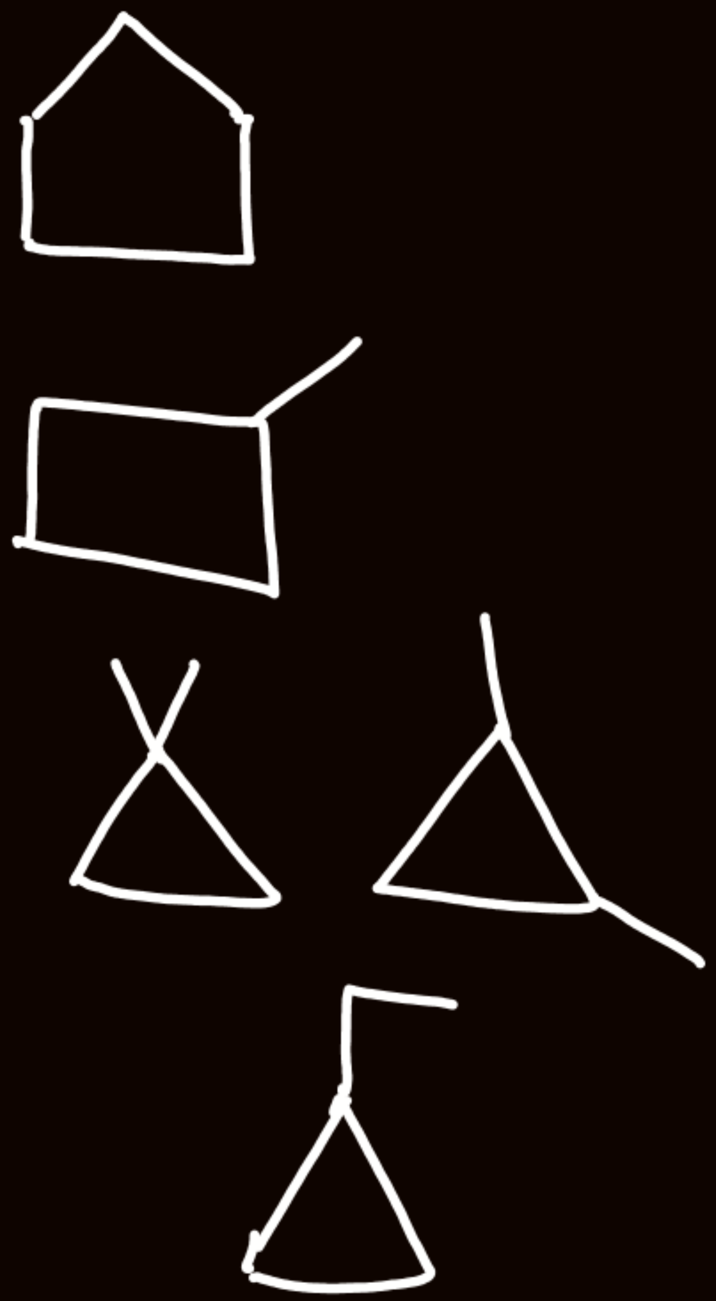
TSI = 5

Cal TSI in C_5H_{10}

DU = 1
- cyclic → 1 Ring
- acyclic → 1 double bond

cyclic = 5
acyclic = 5

cyclic



acyclic

C=C–C–C–C

C–C=C–C–C

C=C–C–C (with C branch on C-2)

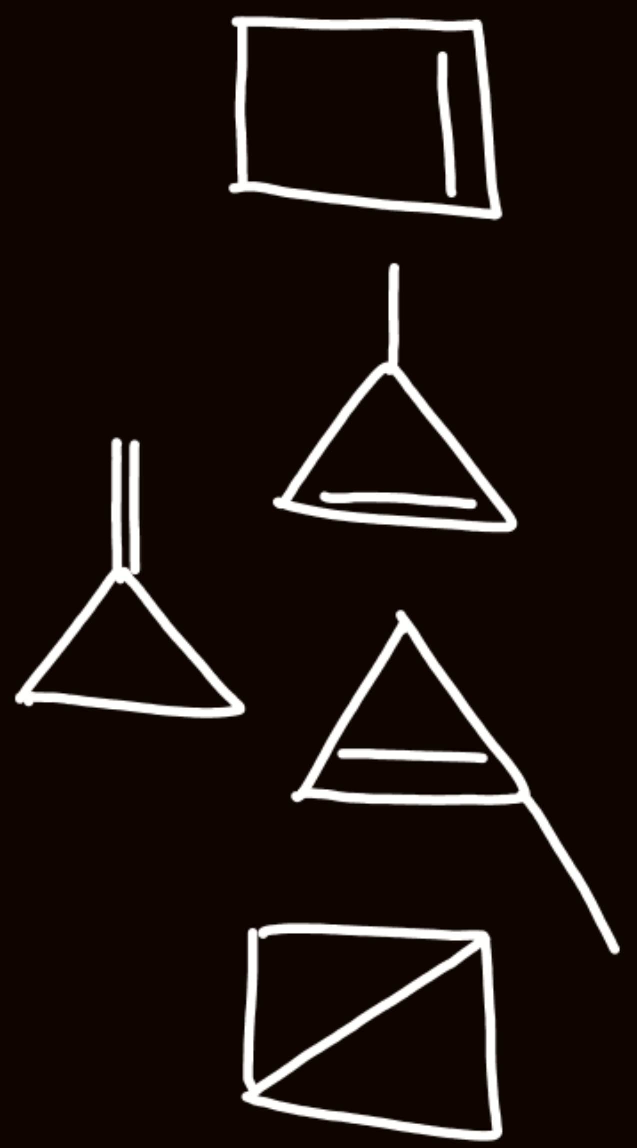
C–C=C–C (with C branch on C-2)

C–C–C=C (with C branch on C-2)

Que Cal TSI in C_4H_6 ?

DU = 2
- cyclic → 2 Ring , 1 Ring + 1 doublebond
- acyclic → 1 triplebond, 2 doublebond

cyclic



acyclic

C≡C–C–C

C–C≡C–C

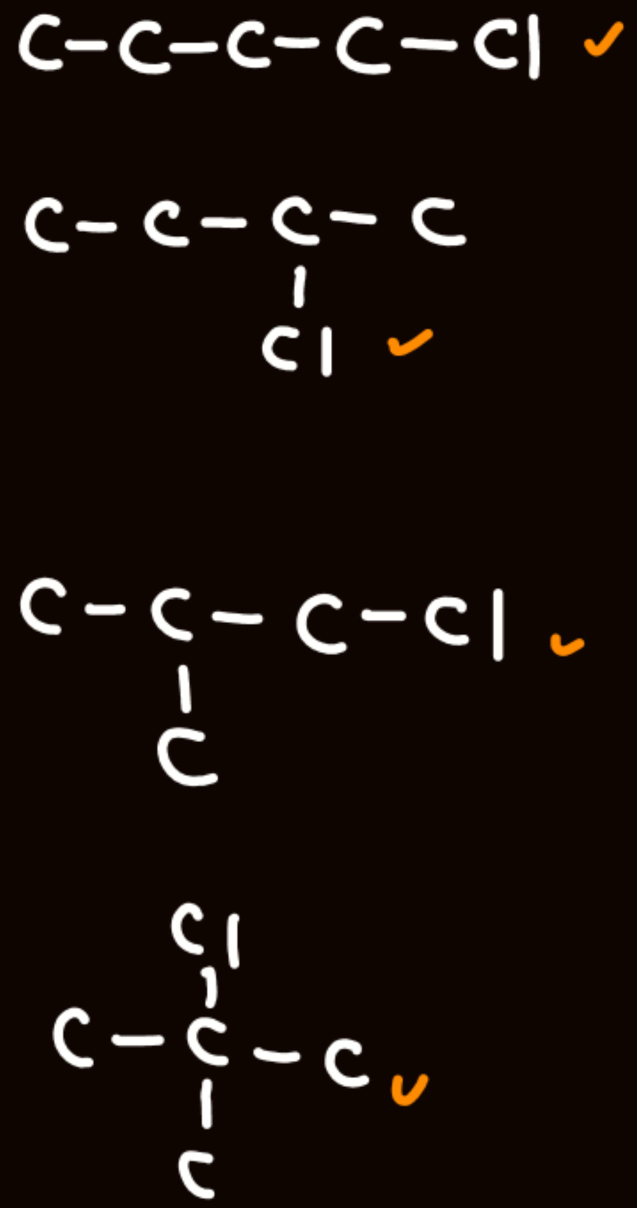
C=C=C–C

C=C–C=C

cyclic isomer = 5
acyclic " = 4

TSI = 9

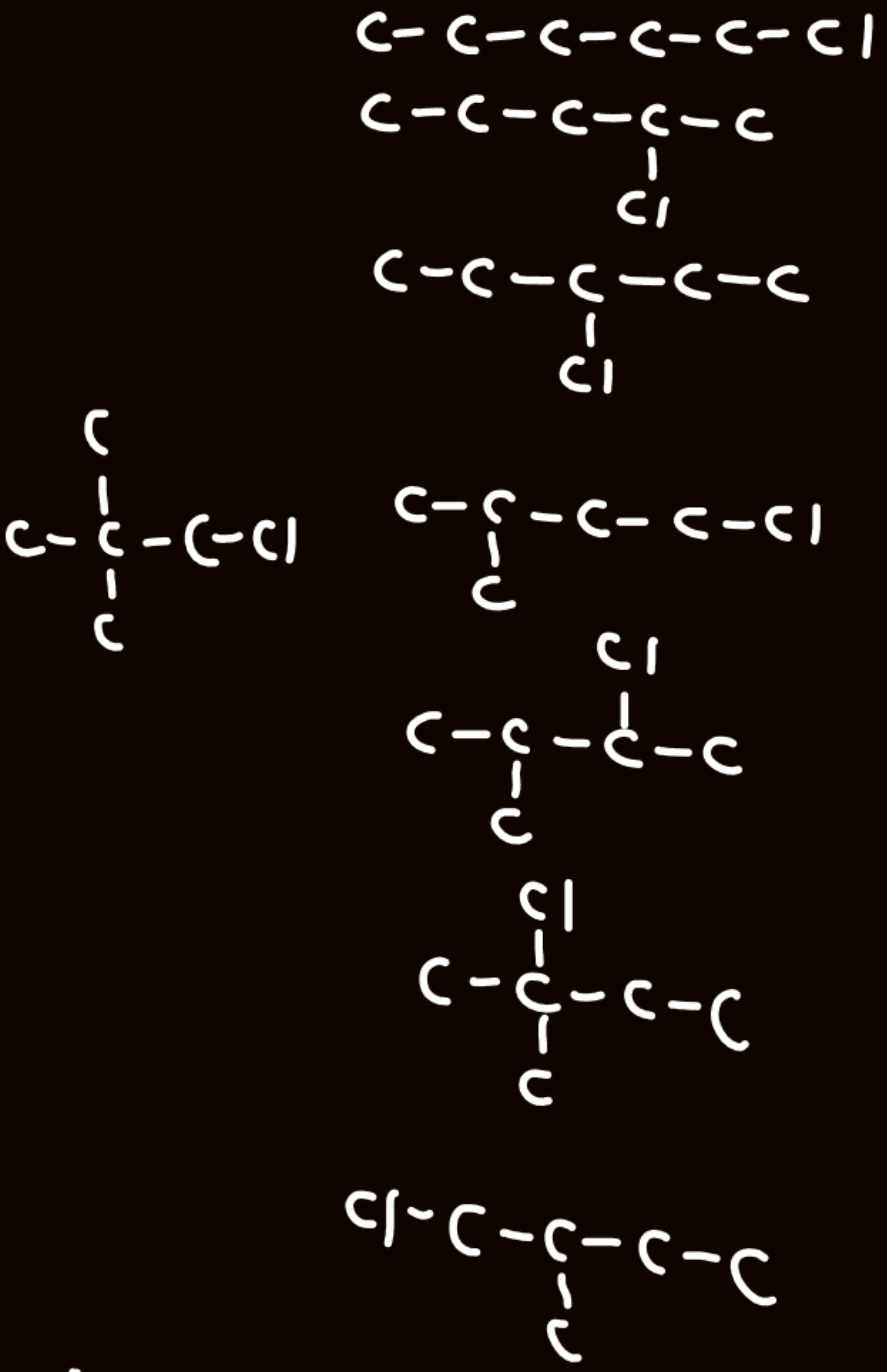
Cal total Monochloroderivative of C_4H_{10} ?



Short trick

$\underbrace{C_4}_{4\,MR}$ —— Cl } 4 monochloroderivative

Que Find total monochloroderivative of C_5H_{10} ?



$C_5 — Cl$

8MR

8 monochloroderivative

Que Find total monochloroderivative of

(i) CH_4 → $\underbrace{C_1}_{1MR}-Cl$ → 1 monochloroderivative

(ii) C_2H_6 → $\underbrace{C_2}_{1MR}-Cl$ → 1 monochloroderivative

(iii) C_3H_8 → $\underbrace{C_3}_{2MR}-Cl$ → 2 monochloroderivative

(iv) C_4H_{10} → $\underbrace{C_4}_{4MR}-Cl$ → 4 " " "

(v) C_5H_{12} → $\underbrace{C_5}_{8MR}-Cl$ → 8 " " "

(vi) C_6H_{14} → $\underbrace{C_6}_{17MR}-Cl$ → 17 " " "

Que Find total structural isomers of $C_4H_{10}O$?

আগে DU = 0 → openchain & single bond

oxy = 1 → alcohol, ether

alcohol

$C_4 — OH$

4MR

↓

4 alcohol isomer

ether

$C_1 — O — C_3$ = 2MR (1MR, 2MR)

$C_2 — O — C_2$ = 1MR (1MR, 1MR)

3 ether isomer

Que Find total Structural isomer of $C_5H_{12}O$.   **TSI = 14**

DU = 0
oxy = 1

alcohol

ether

alcohol

C_5 — OH

8 MR

↓

8 alcohol isomer

ether

C_1 — O — C_4 = 4MR

1MR   4MR

C_2 — O — C_3 = 2MR

1MR   2MR

6 ether isomer

Q) Find aldehyde & ketone isomer of C_4H_8O

DU = 1, oxy = 1 } aldehyde, ketone

aldehyde

C_3 — CHO

(C_3 = 2MR)

↓

2 aldehyde isomer

Ketone

C_1 — C(=O) — C_2

(C_1 = 1MR, C_2 = 1MR) = 1MR

1 ketone isomer

TSI = 3

Q Cal Carboxylic acid & Ester isomers of $C_4H_8O_2$.

DU = 1, oxy = 2] Carboxylic acid, Ester

Utsiv official

$R/H-\overset{O}{\overset{||}{C}}-O-R$

Carboxylic acid

C_3-COOH

2MR

↓

2 isomer

Ester

$H-\overset{O}{\overset{||}{C}}-O-C_3$ = 2 (2MR)

$C-\overset{O}{\overset{||}{C}}-O-C_2$ = 1 (1, 1)

$C-C-\overset{O}{\overset{||}{C}}-O-C$ = 1 (1, 1)

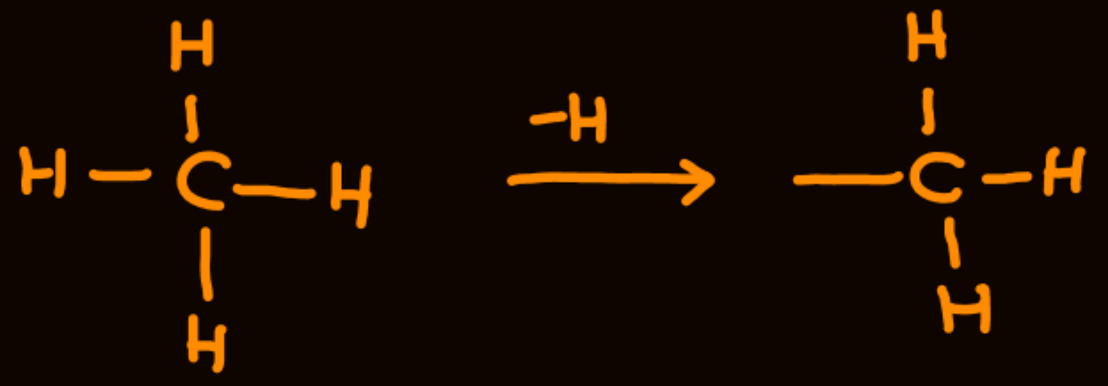
4 isomer

Calculation of Monovalent Radical (MR)

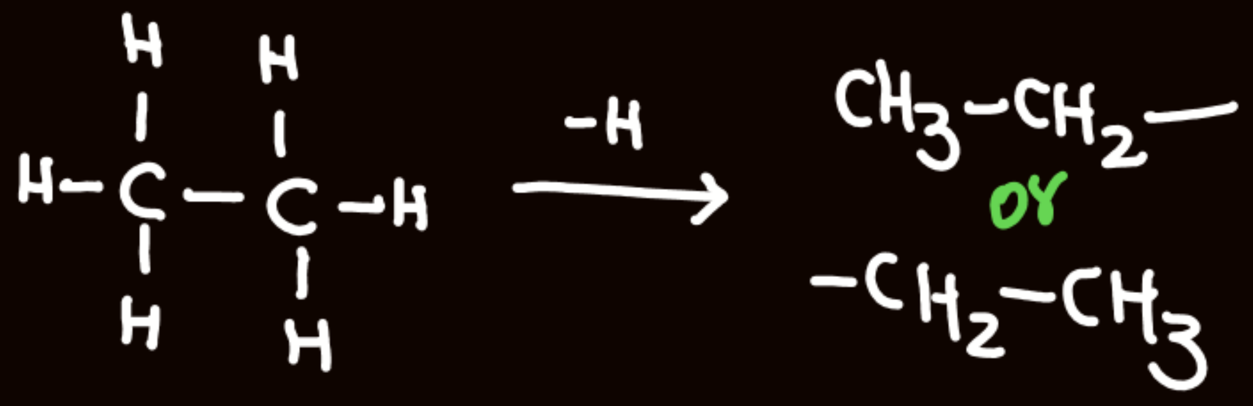
- Monovalent → Removal of one Hydrogen
- Radical → Comp formed after removal of Hydrogen

Monovalent Radical (MR) → Comp formed after removal of one Hydrogen is MR.

Que Cal total num of monovalent Radical in CH_4 → 1 MR



Que Cal total num of monovalent Radical in C_2H_6



→ 1 MR

Que Cal MR in C_3H_8

$CH_3-CH_2-CH_3$ (2°, 1°) → $CH_3-CH_2-CH_2-$ npropyl ; $CH_3-\underset{|}{CH}-CH_3$ isopropyl } 2MR

Que Cal MR in C_4H_{10} → **4 MR**

$CH_3-CH_2-CH_2-CH_3$ nbutane (2°, 1°) →

C–C–C–C– nbutyl

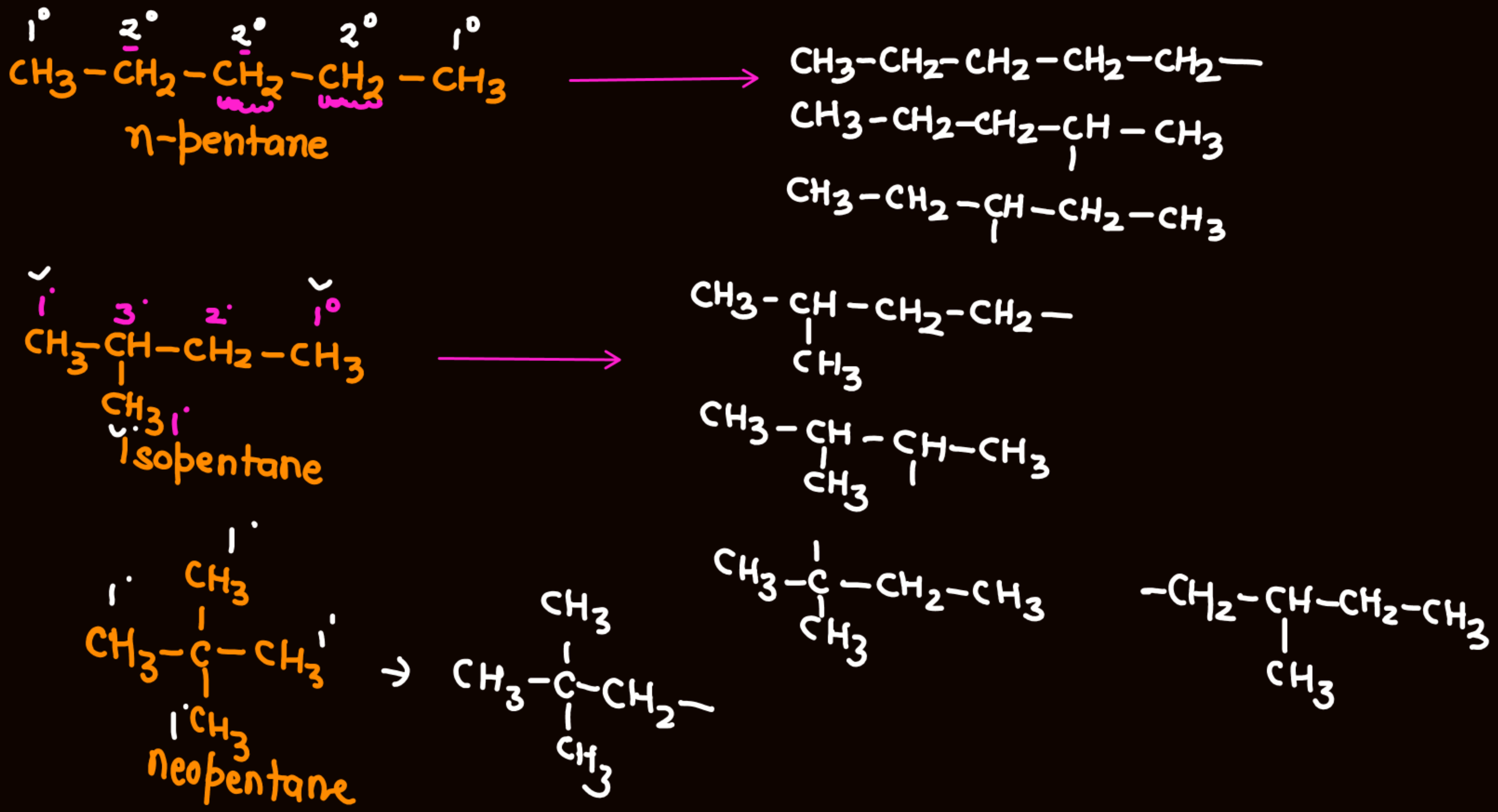
C–C–C(–)–C Secbutyl

C–C(C)–C– isobutyl

C–C(C)(–)–C tertbutyl

$CH_3-\underset{CH_3}{CH}-CH_3$ (1°, 3°, 1°) isobutane

Q C_5H_{12} → MR ?? → 8MR



Monovalent Radical Table

MR-Table

CH_4 →	1
C_2H_6 →	1
C_3H_8 →	2
C_4H_{10} →	4
C_5H_{12} →	8
* C_6H_{14} →	17

Calculation of Total Structural Isomer (TSI)

Que Cal TSI in CH_4.

Step 1 → DU $= (C+1) - \left(\frac{H+X-N}{2}\right)$

$= 2 - \left(\frac{4+0-0}{2}\right)$

$= 0$

CH_4

→ donot show structural isomerism.

Que2 Cal TSI in C_2H_6

DU $= 3 - \left(\frac{6}{6}\right) = 0$ → openchain & Singlebond

CH_3-CH_3

→ donot show structural isomer.

Que Cal TSI in C_3H_8

DU $= 0$ openchain & Singlebond

$CH_3-CH_2-CH_3$

→ donot show structural isomerism.

Que Cal TSI in C_4H_{10}.

DU $= 0$ openchain & Singlebond

$CH_3-CH_2-CH_2-CH_3$

$CH_3-CH(CH_3)-CH_3$

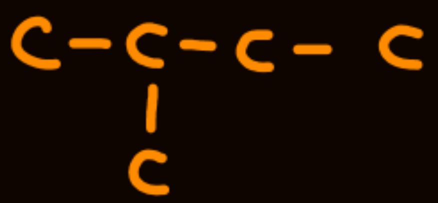
} 2 TSI

Que Cal TSI in C_5H_{12} → 3 TSI

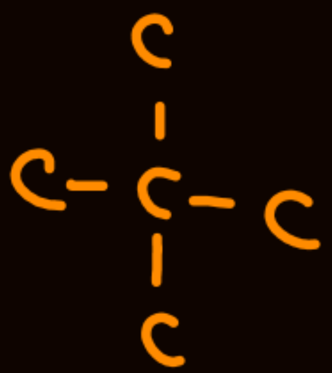
DU = 0 openchain & Single bond



npentane



isopentane



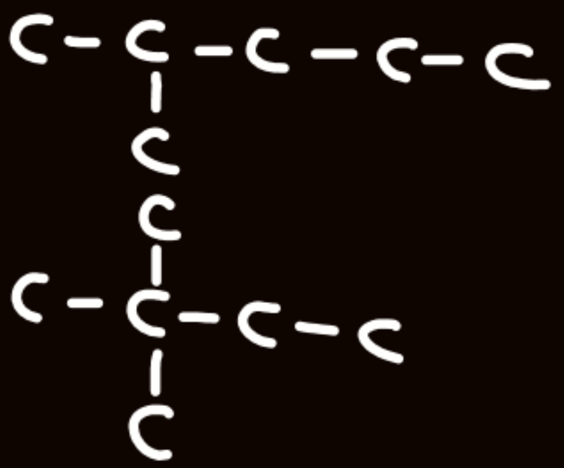
neopentane

C_6H_{14} → 5 TSI

DU = 0

openchain & Single bond





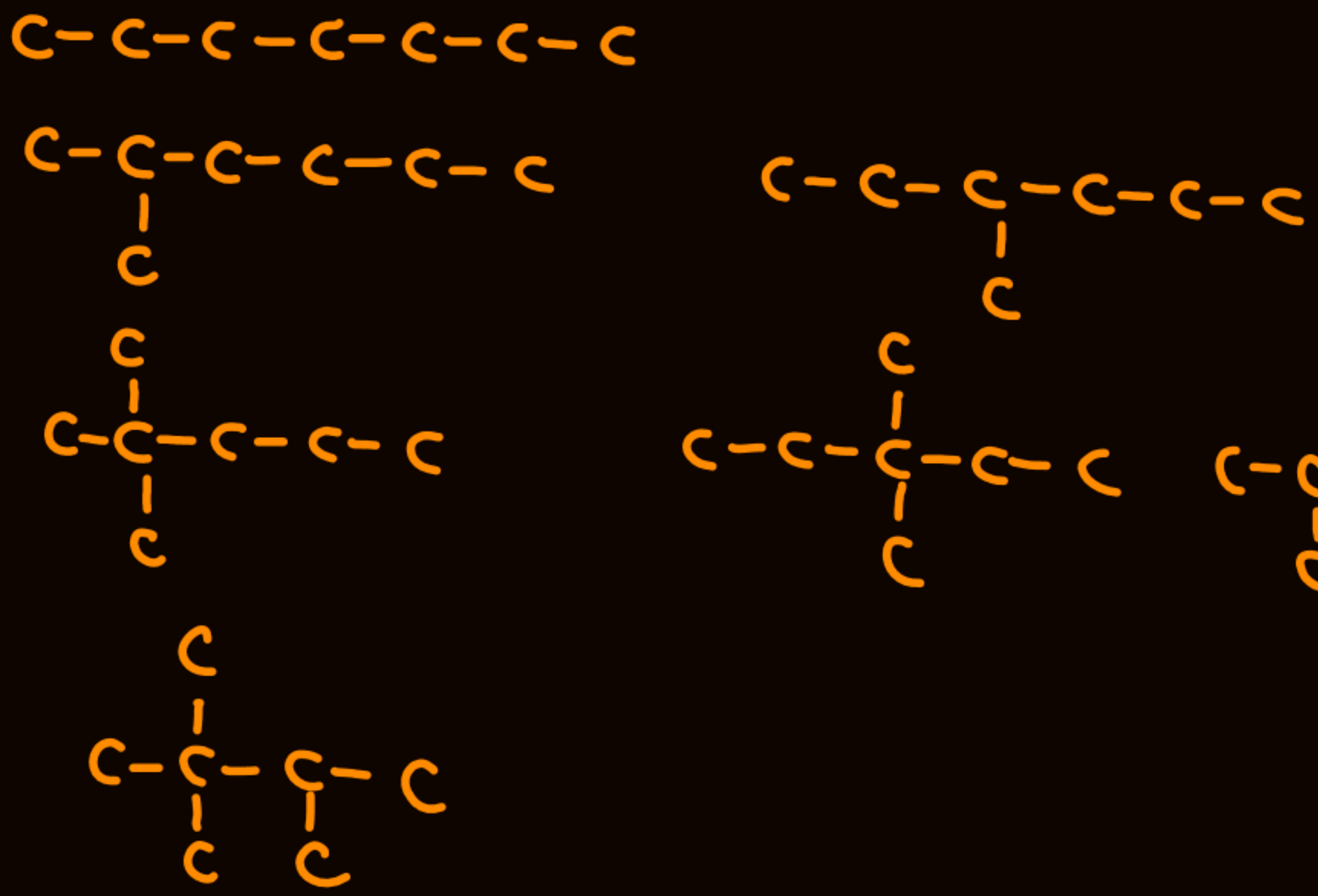


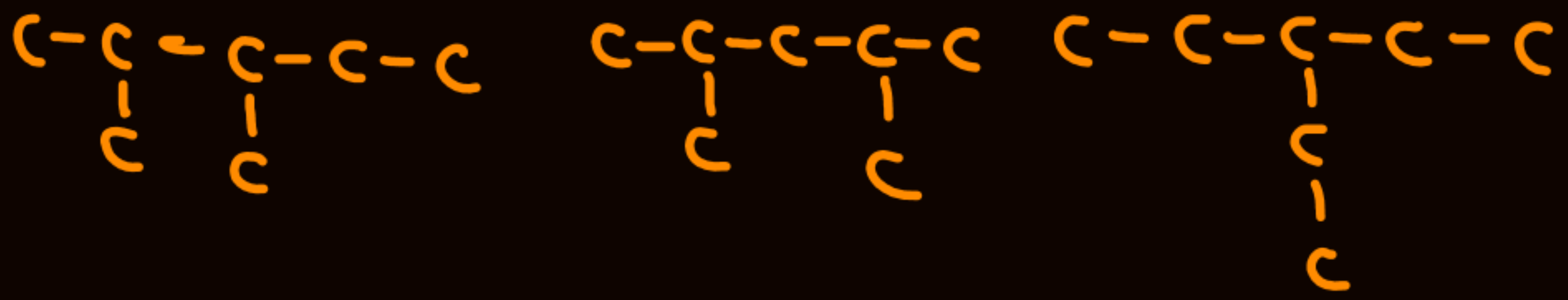


Q C_7H_{16} TSI ?? ⟶ 9 TSI

DU = 0

open chain & Singlebond





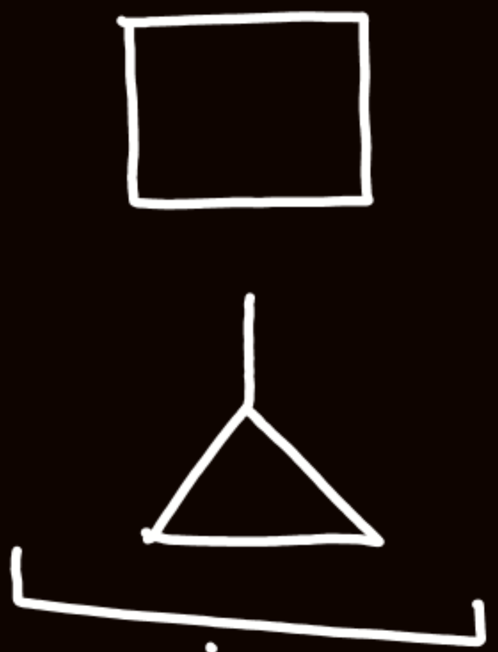
Alkane ↳

Comp	TSI
CH_4	0
C_2H_6	0
C_3H_8	0
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9

Que Cal TSI in C_4H_8

DU = 1 → cyclic → 1 Ring
↳ acyclic → 1 double bond

cyclic



2 isomer

acyclic

C=C–C–C

C–C=C–C

C–C=C
    |
    C

3 Isomer

Cyclic isomer – 2
acyclic " → 3

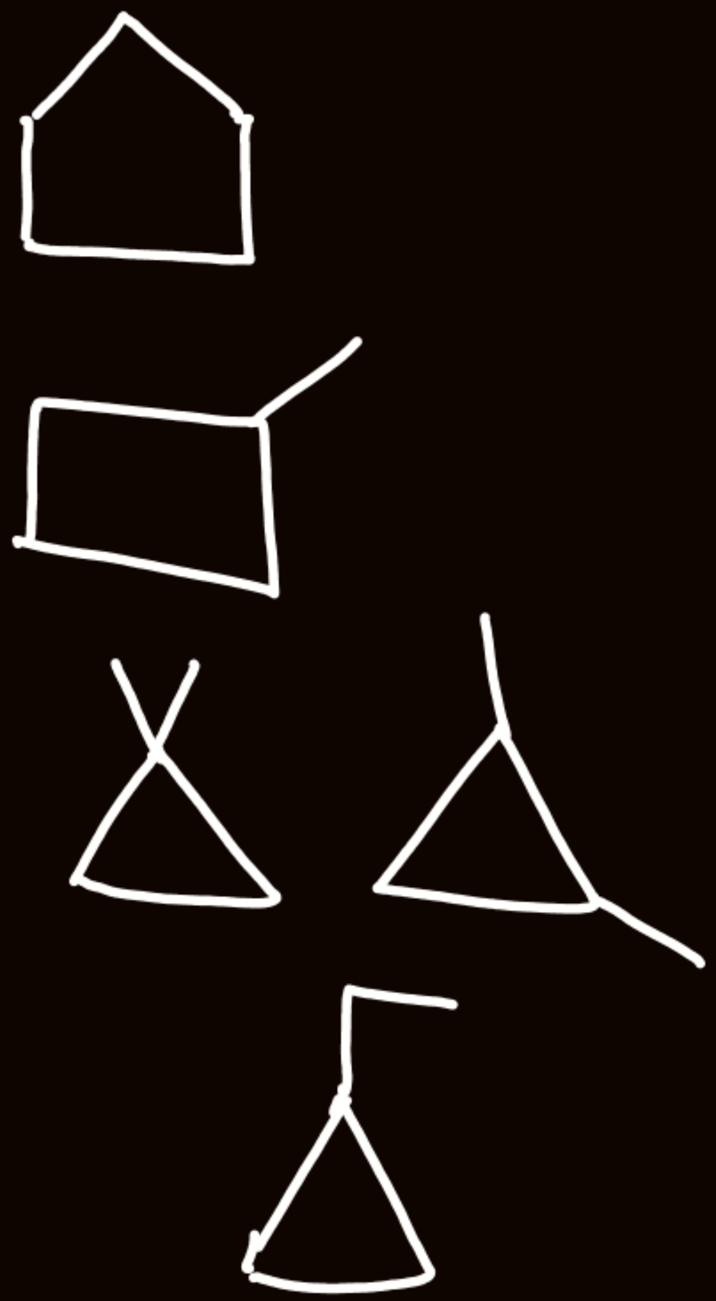
TSI = 5

Cal TSI in C_5H_{10}

DU = 1
- cyclic → 1 Ring
- acyclic → 1 double bond

cyclic = 5
acyclic = 5

cyclic



acyclic

C=C–C–C–C

C–C=C–C–C

C=C(–C)–C–C

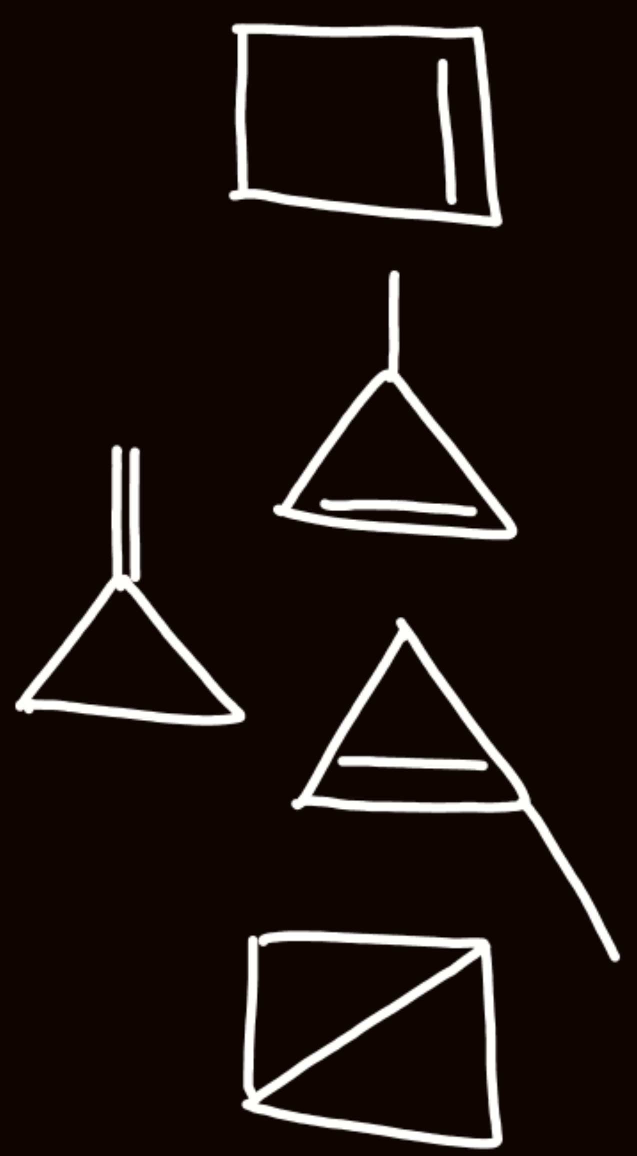
C–C(–C)=C–C

C–C(–C)–C=C

Que Cal TSI in C_4H_6 ?

DU = 2
- cyclic → 2 Ring, 1 Ring + 1 double bond
- acyclic → 1 triple bond, 2 double bond

cyclic



acyclic

C≡C–C–C

C–C≡C–C

C=C=C–C

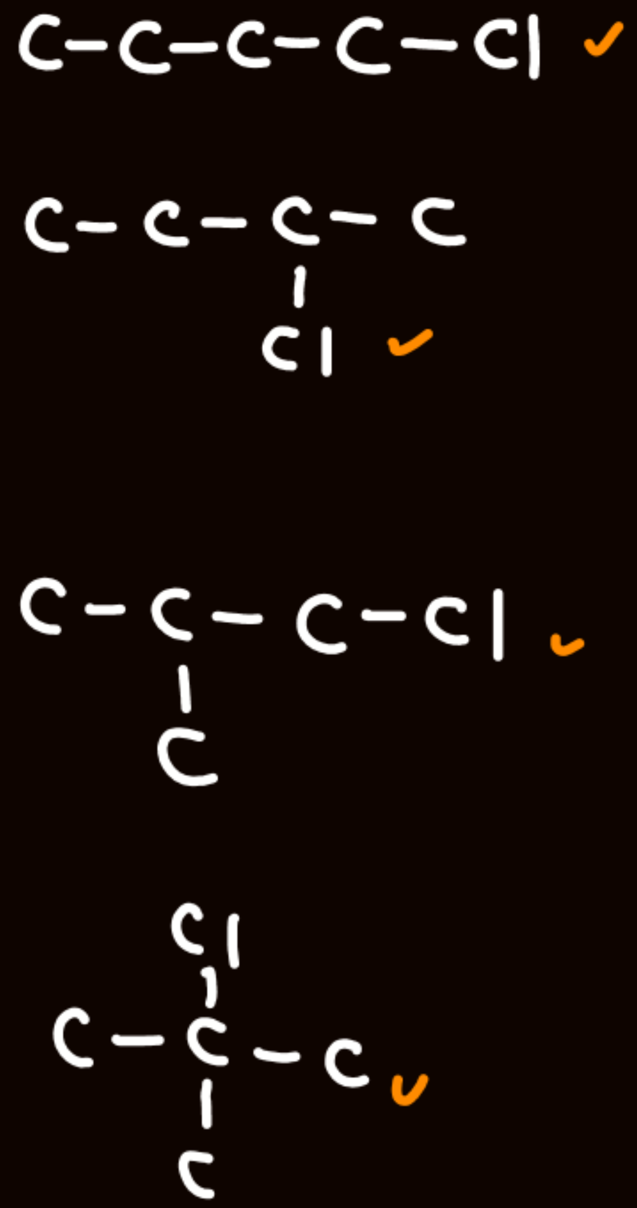
C=C–C=C

cyclic isomer = 5

acyclic " = 4

TSI = 9

Cal total Monochloroderivative of C_4H_{10} ?

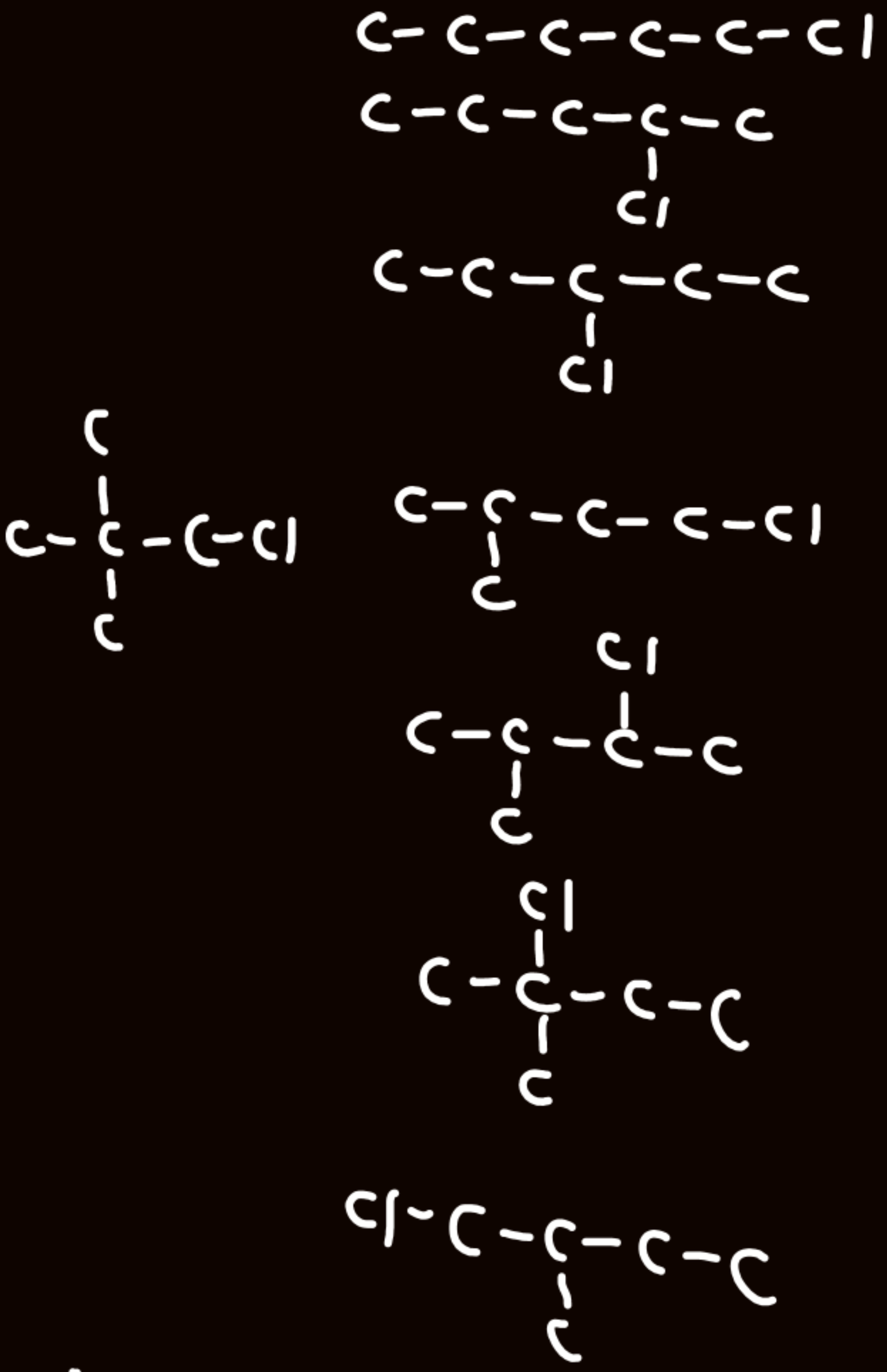


Short trick

C_4 — Cl } 4 monochloroderivative

4 MR

Que Find total monochloroderivative of C_5H_{10} ?



$C_5 — Cl$

8MR

8 monochloroderivative

Que Find total monochloroderivative of

(i) CH_4 → $\underbrace{C_1}_{1MR}-Cl$ → 1 monochloroderivative

(ii) C_2H_6 → $\underbrace{C_2}_{1MR}-Cl$ → 1 monochloroderivative

(iii) C_3H_8 → $\underbrace{C_3}_{2MR}-Cl$ → 2 monochloroderivative

(iv) C_4H_{10} → $\underbrace{C_4}_{4MR}-Cl$ → 4 " " "

(v) C_5H_{12} → $\underbrace{C_5}_{8MR}-Cl$ → 8 " " "

(vi) C_6H_{14} → $\underbrace{C_6}_{17MR}-Cl$ → 17 " " "

Que Find total structural isomers of $C_4H_{10}O$?

আগে

DU = 0
oxy = 1

openchain & single bond

→ alcohol

→ ether

alcohol

C_4 — OH

4MR

↓

4 alcohol isomer

ether

C_1 — O — C_3 = 2MR

1MR, 2MR

C_2 — O — C_2 = 1MR

1MR, 1MR

3 ether isomer

Que Find total Structural isomer of $C_5H_{12}O$.   **TSI = 14**

DU = 0
oxy = 1

alcohol

ether

alcohol

C_5 — OH

8 MR

↓

8 alcohol isomer

ether

C_1 — O — C_4 = 4MR

1MR   4MR

C_2 — O — C_3 = 2MR

1MR   2MR

6 ether isomer

Q) Find aldehyde & ketone isomer of C_4H_8O

DU = 1 } aldehyde
oxy = 1 } ketone

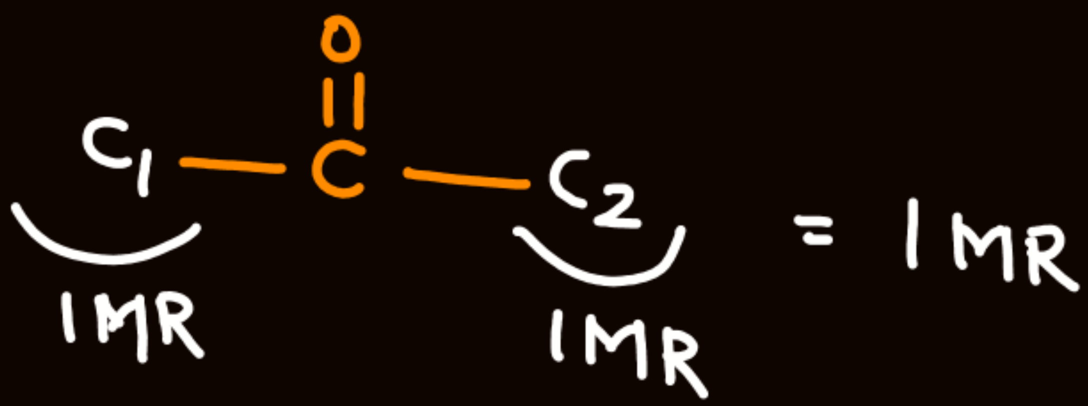
aldehyde



↓

2 aldehyde isomer

Ketone



1 ketone isomer

TSI = 3

Q Cal Carboxylic acid & Ester isomers of $C_4H_8O_2$.

DU = 1, oxy = 2] Carboxylic acid / Ester

R/H — C(=O) — O — R

Carboxylic acid

C_3 — COOH

C_3 : 2MR

↓

2 isomer

Ester

H — C(=O) — O — C_3 = 2 (C_3: 2MR)

C — C(=O) — O — C_2 = 1 (1 × 1)

C — C — C(=O) — O — C = 1 (1 × 1)

4 isomer

Calculation of Total Structural Isomer

Que Cal TSI of $C_4H_8O_2$ containing Carboxylicacid ??

Cal TSI of $C_4H_8O_2$ " Ester ??

$DU = 1$
$oxy = 2$

Carboxylicacid

Ester

Carboxylic acid

C_3 —— COOH

2MR

↓

2TSI

Carboxylic Acid

Ester

H—C(=O)—O—C_3 = 2 TSI

2MR

C_1—C(=O)—O—C_2 = 1 MR = 1 TSI

1MR 1MR

C_2—C(=O)—O—C_1 = 1MR = 1 TSI

1MR 1MR

4 TSI Ester

Que Cal TSI of $C_4H_{11}N$ containing 1° amine
Cal TSI of $C_4H_{11}N$ 〃 2° amine
Cal TSI of $C_4H_{11}N$ 〃 3° amine

Total TSI = 8

DU = 0 Nitrogen = 1	1° amine 2° amine 3° amine

1° amine

$C_4 — NH_2$

4MR

↓

4 TSI 1° amine

2° amine

$C_1 — NH — C_3$ = 2MR

(1MR, 2MR)

$C_2 — NH — C_2$ = 1MR

(1MR, 1MR)

3MR

3 TSI 2° amine

3° amine

C_1 (1MR)
|
$C_1 — N — C_2$

(1MR, 1MR)

= 1MR

= 1 TSI 3° amine

Que
neet
2016
PYQ

Cal TSI of $C_6H_{15}N$ Containing 3° amine?

3° amine

$C_1 - N - C_4$ (with C_1 on N); C_1: 1MR, C_4: 4MR, C_1: 1MR = 4 TSI

$C_1 - N - C_3$ (with C_2 on N); C_1: 1MR, C_3: 2MR, C_2: 1MR = 2 TSI

$C_2 - N - C_2$ (with C_2 on N); C_2: 1MR, C_2: 1MR, C_2: 1MR = 1 TSI

7 TSI

1° amine

$C_6 - NH_2$; C_6: 17MR

↓

17 TSI

2° amine

$C_1 - NH - C_5$; 1, 8 = 8 TSI

$C_2 - NH - C_4$; 1, 4 = 4 TSI

$C_3 - NH - C_3$; 2, 2 = 4 TSI

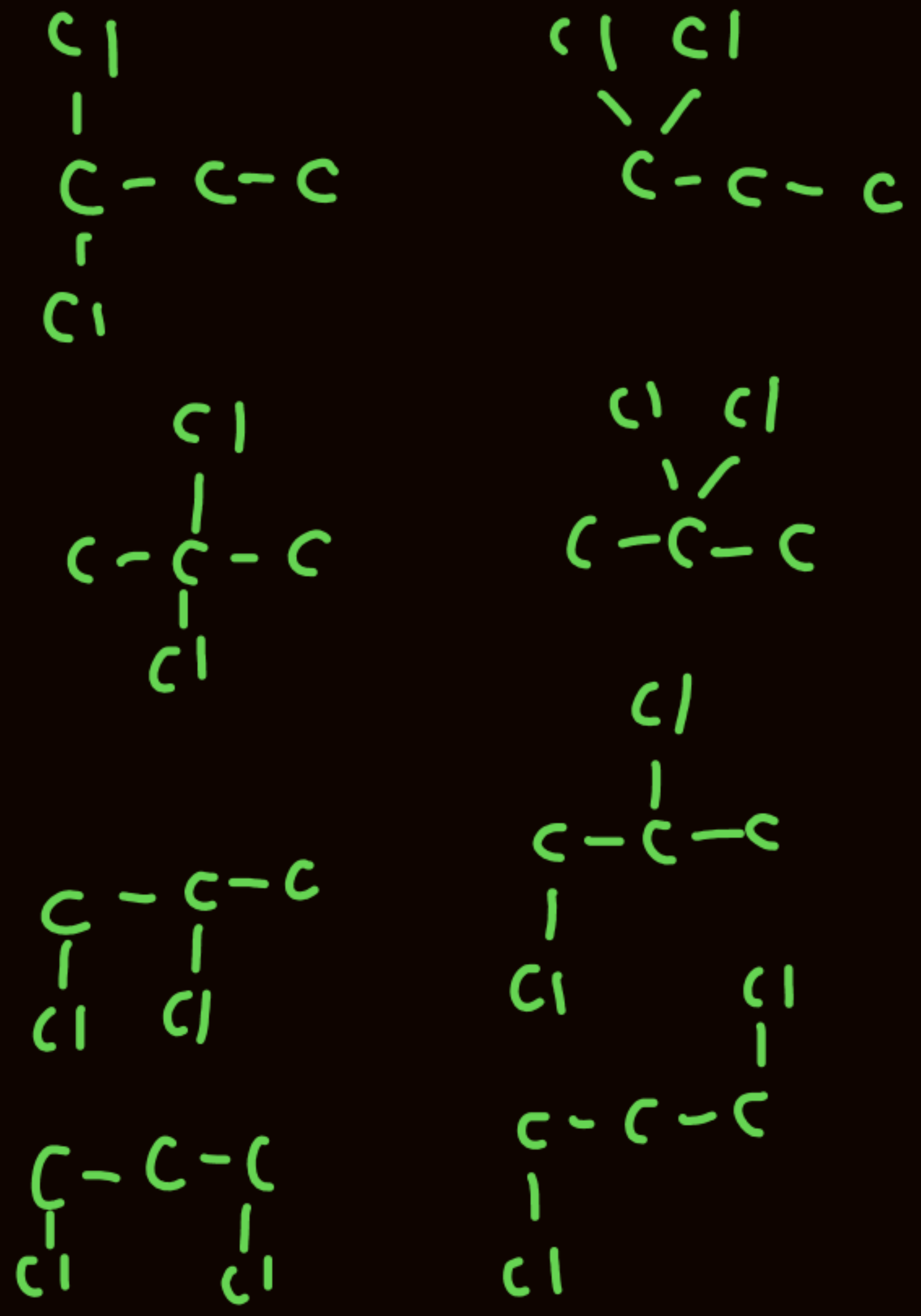
16 TSI

Que Cal TSI of $C_3H_6Cl_2$?? (Bivalent Radical) → MR → not applicable

DU=0 openchain & Single bond

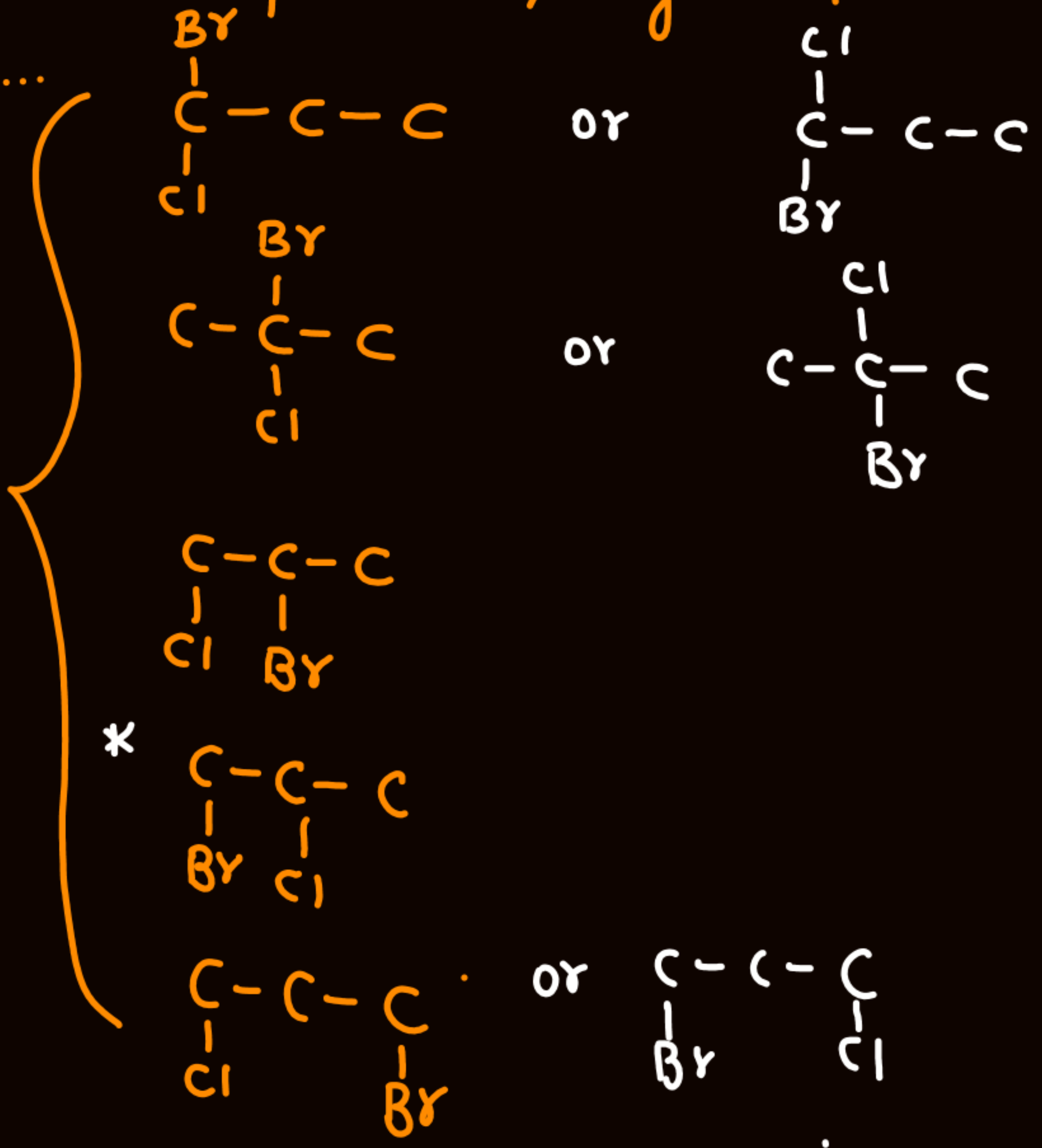


4 TSI



Que Cal TSI of C_3H_6ClBr ??

..... DU = 0 open chain & Single bond



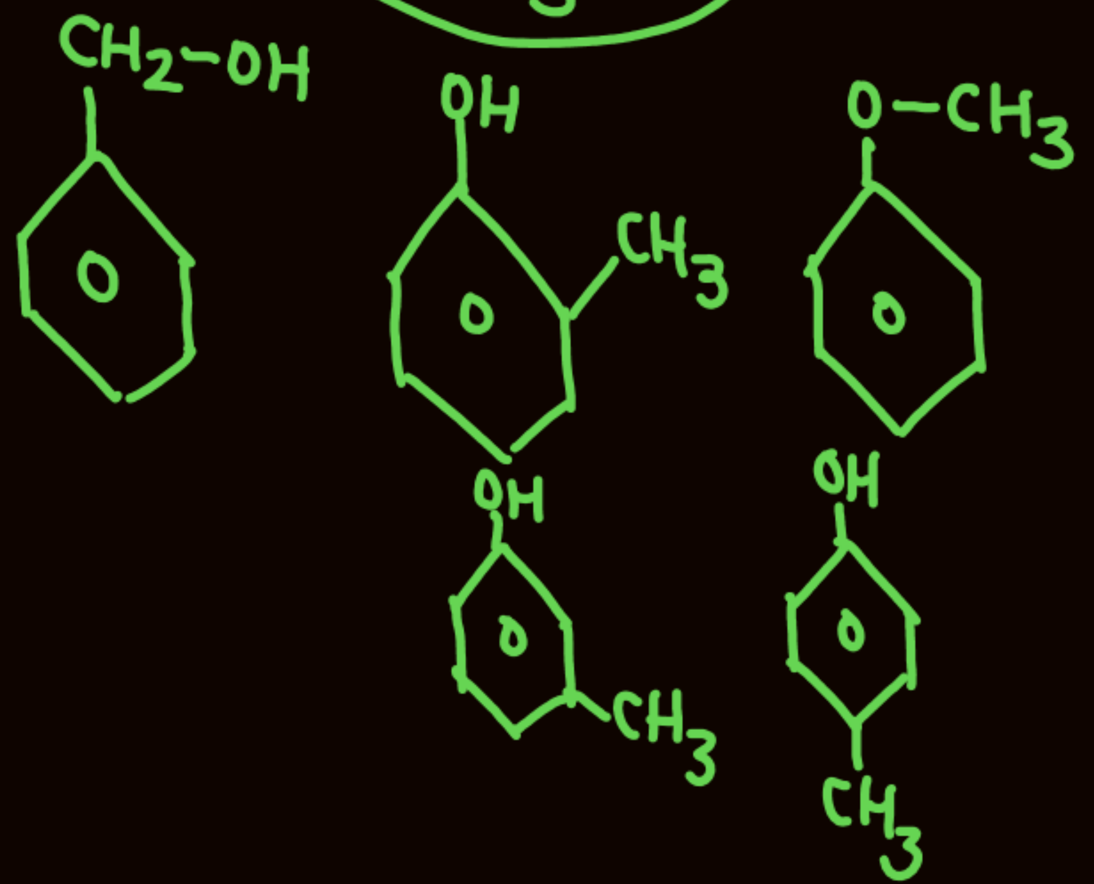
5 TSI

Que Cal total benzenoid isomer of C_7H_8O

Must contain Benzene

Jadu → Subtract Benzene Radical
↳ phenyl
↳ C_6H_5-

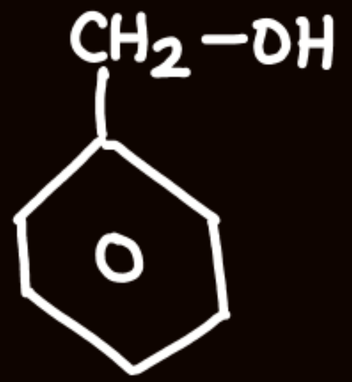
$$\begin{array}{r} C_7H_8O \\ -C_6H_5 \\ \hline CH_3O \end{array}$$



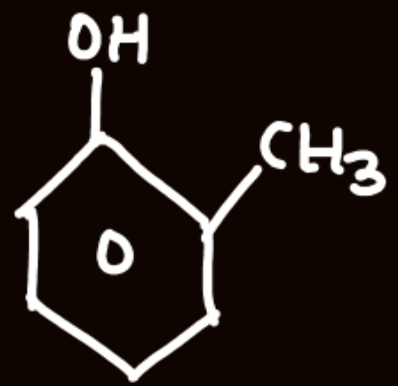
5 TSI

Que cal total Benzenoid isomer of C_7H_8O??

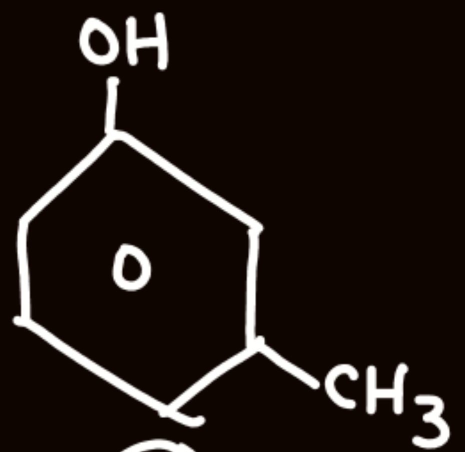
$$\begin{array}{r} C_7H_8O \\ -\ C_6H_5 \\ \hline CH_3O \end{array}$$ C



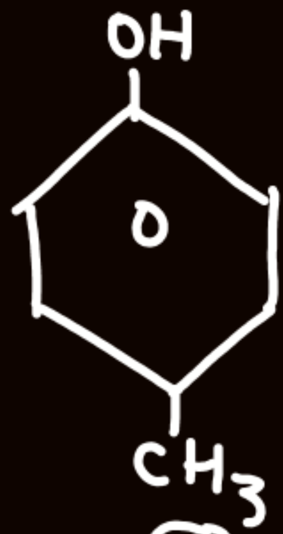
①



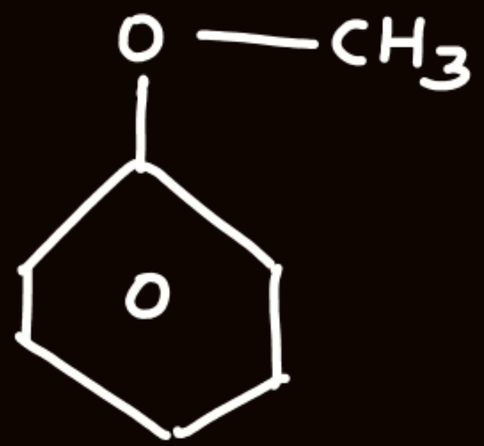
②



③



④



⑤

1,2 → FI
1,3 → FI
1,4 → FI
1,5 → FI

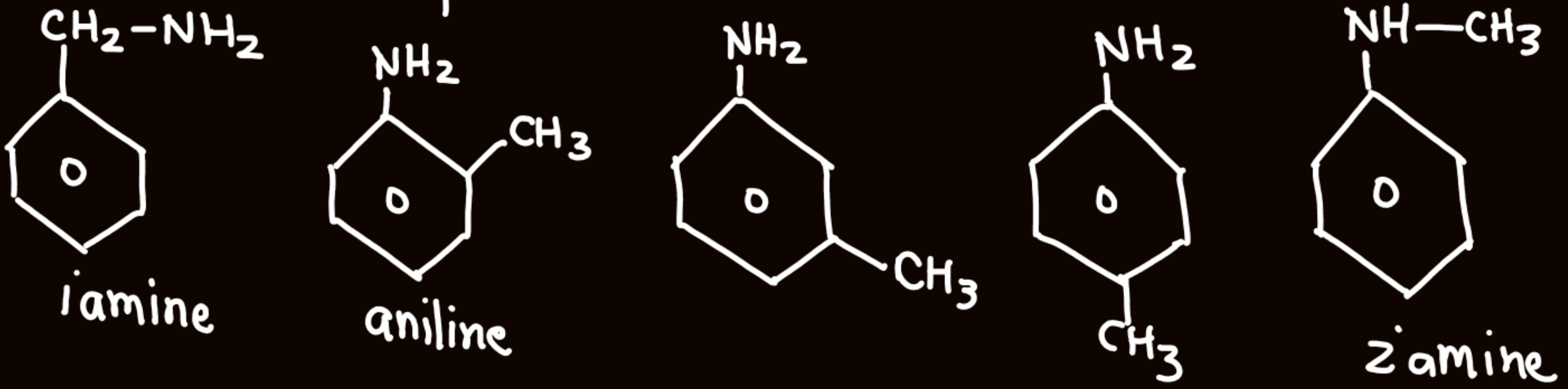
2,3 – PI
2,4 – PI
2,5 – FI

3,4 – PI
3,5 – FI

4,5 – FI

Que Cal total Benzenoid isomer of C_7H_9N ?

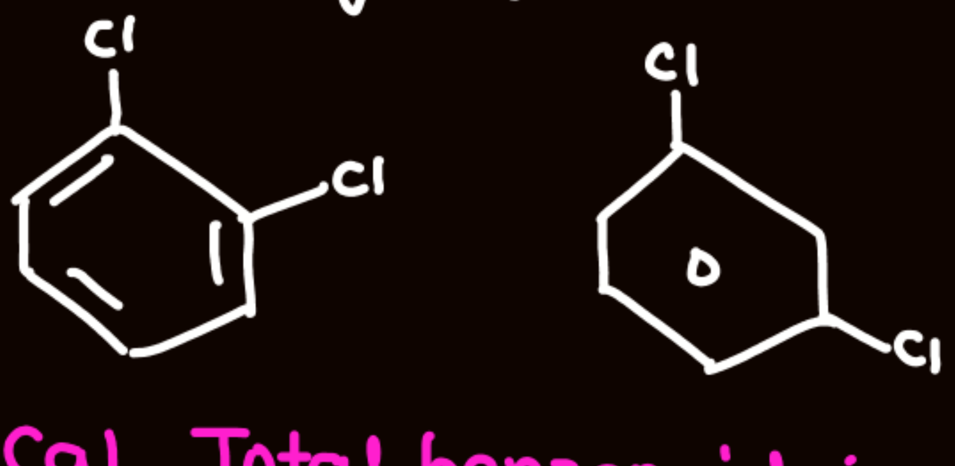
$$\begin{array}{r} C_7H_9N \\ -\,C_6H_5 \\ \hline CH_4N \end{array}$$

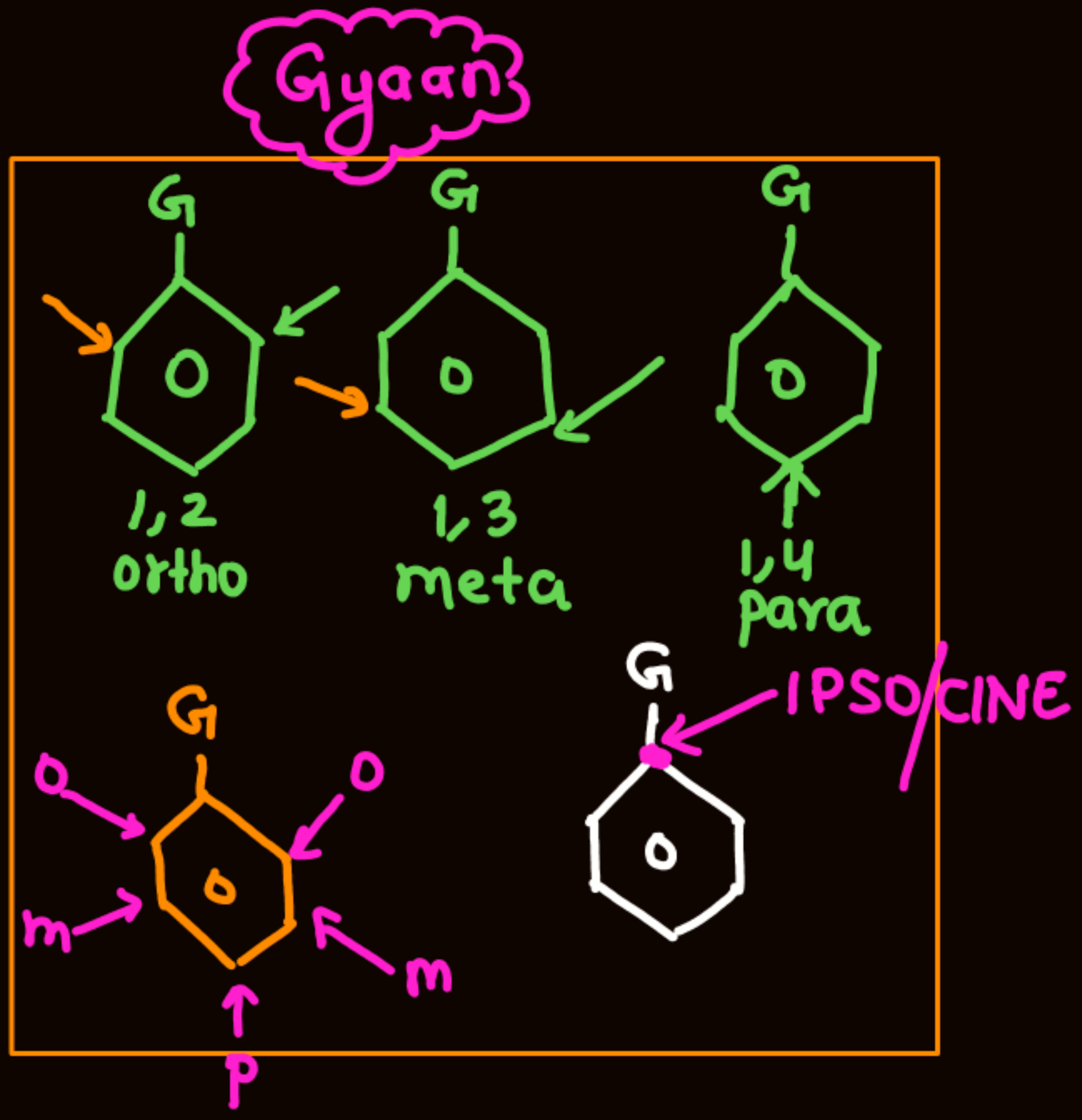


5 Ts|

Que Cal TSI of $C_6H_4Cl_2$ — (Benzenoid isomer)

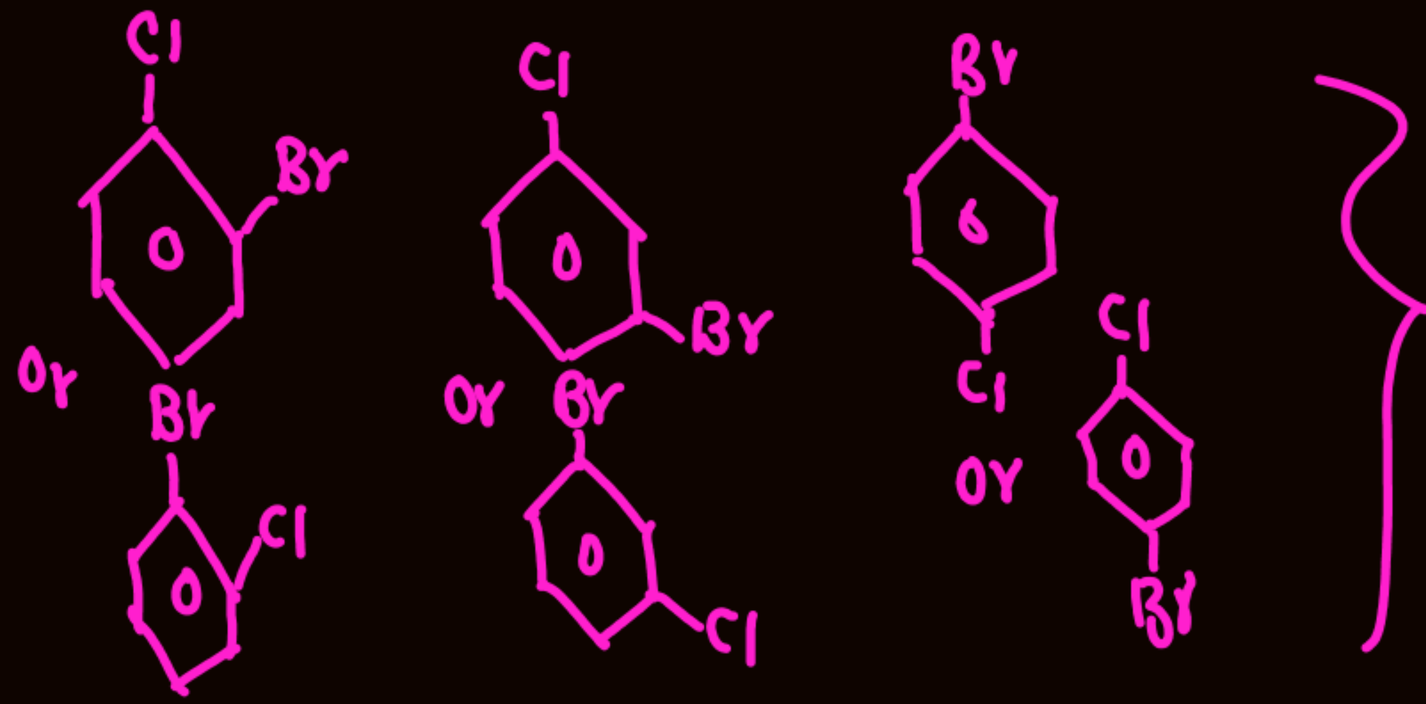
Step 1 : DU = 4
↳ Benzene
(in your Syllabus)





Que Cal Total benzenoid isomer of C_6H_4ClBr

DU = 4 → Benzene

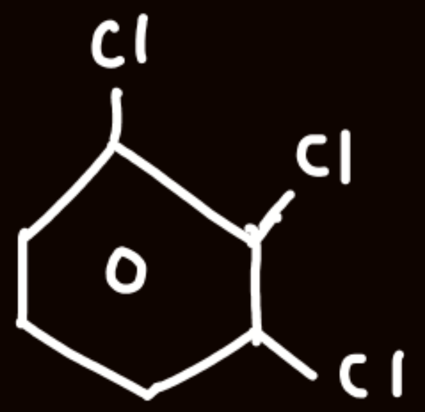


3 Benenzoid isomer

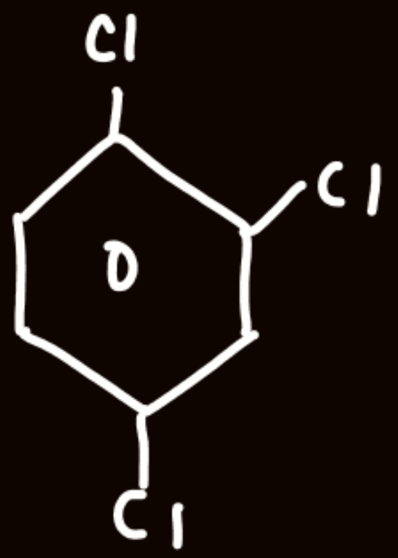
Que cal total benzenoid isomer of $C_6H_3Cl_3$?? → 3 TSI

DU = 4

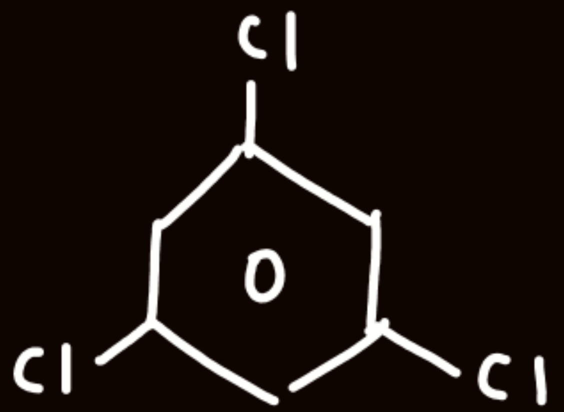
↳ Benzene



1,2,3



1,2,4

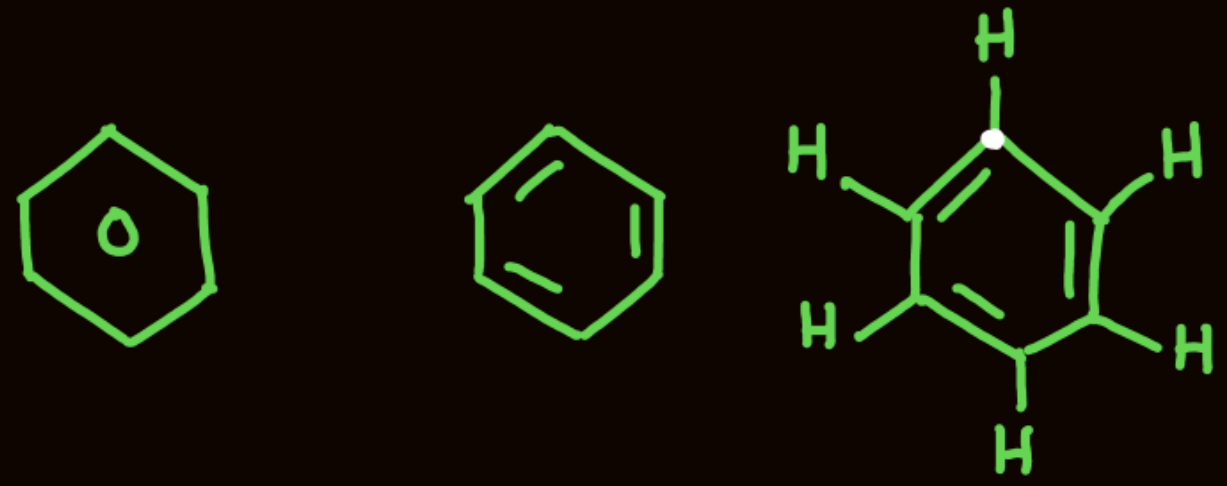


1,3,5

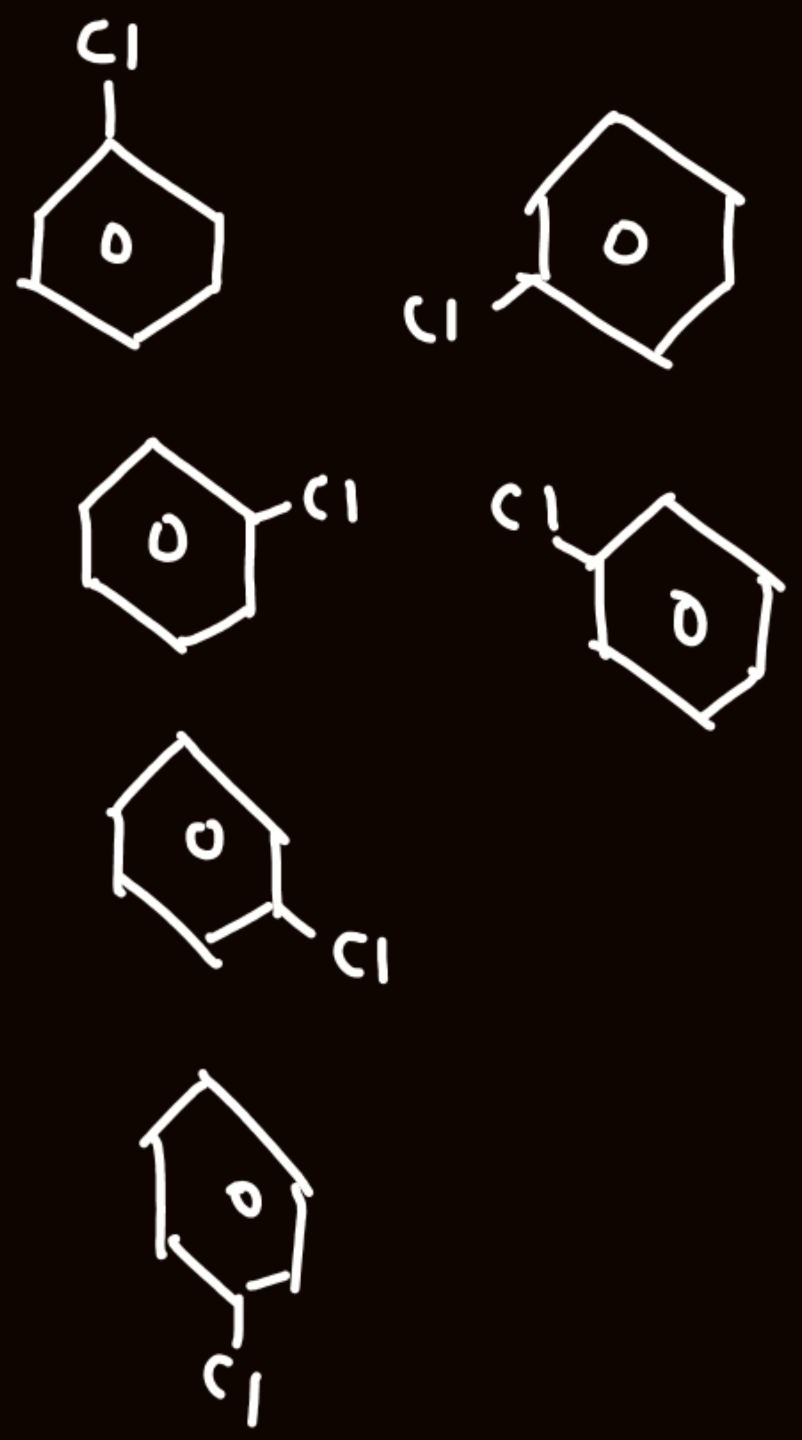
Calculation of monochloro derivative (Mcd)

Que Cal total num of monochloroderivative in Benzene ??

⇒



Ans → 1 monochloroderivative



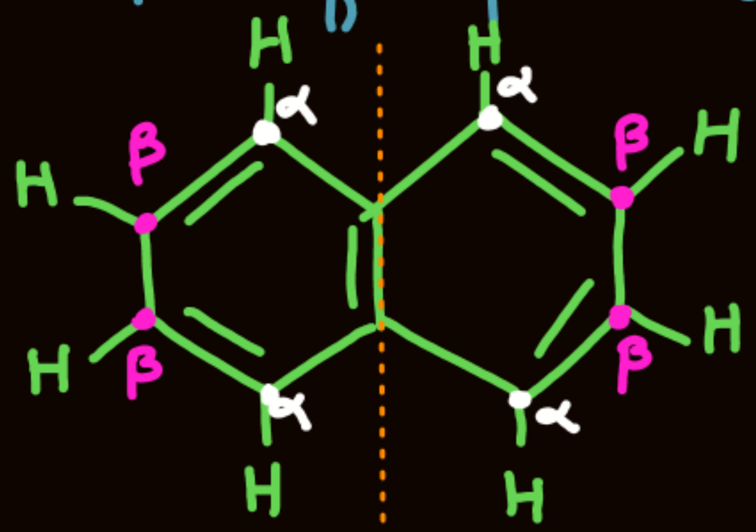
Jadu



all Hydrogen Same
↓
1 Mcd

Que Cal total monochloro derivative of nepthalene ??

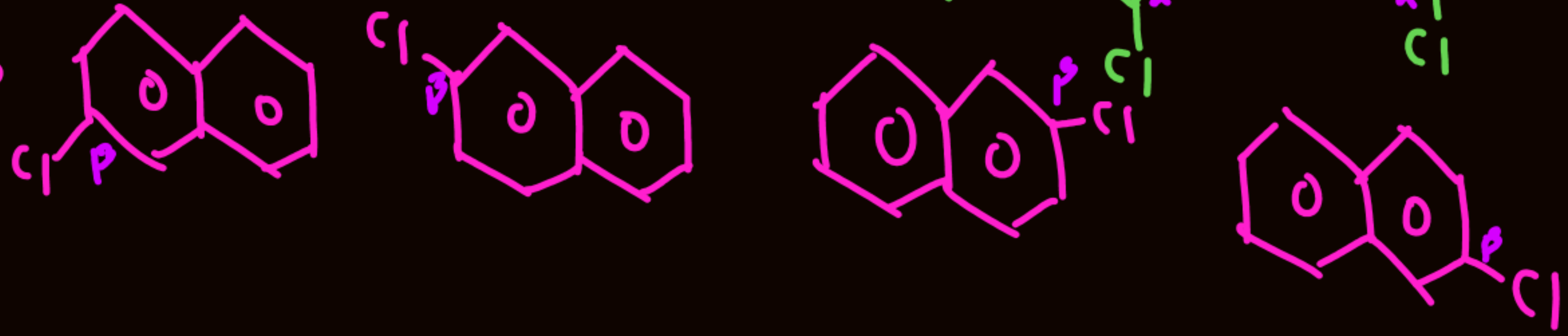




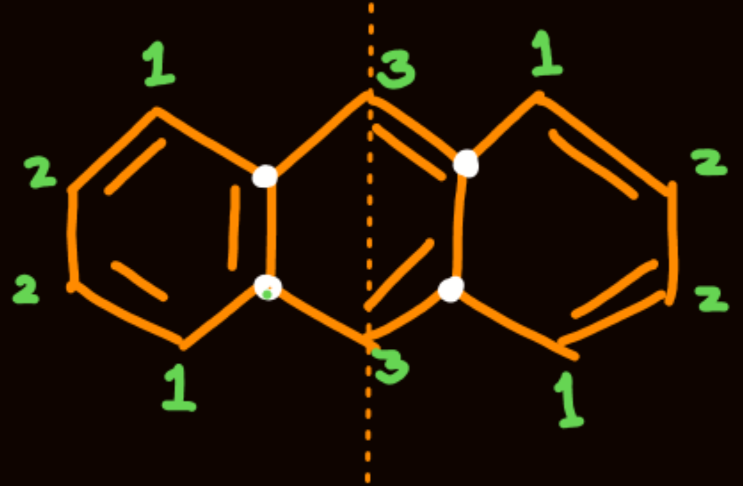
1 →



2 →

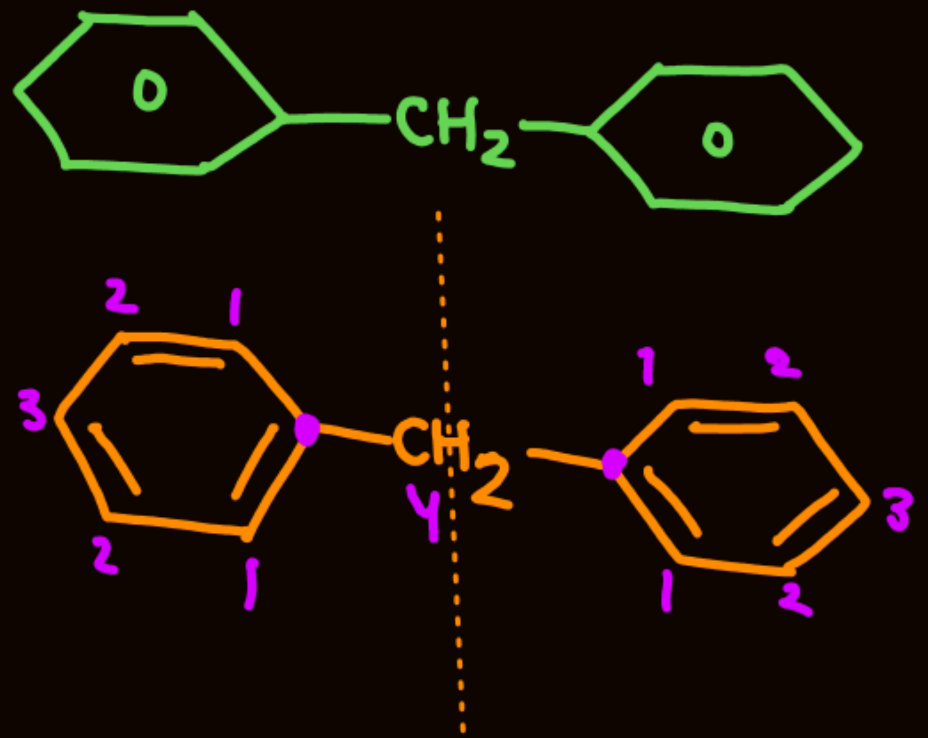


Q Anthracene –



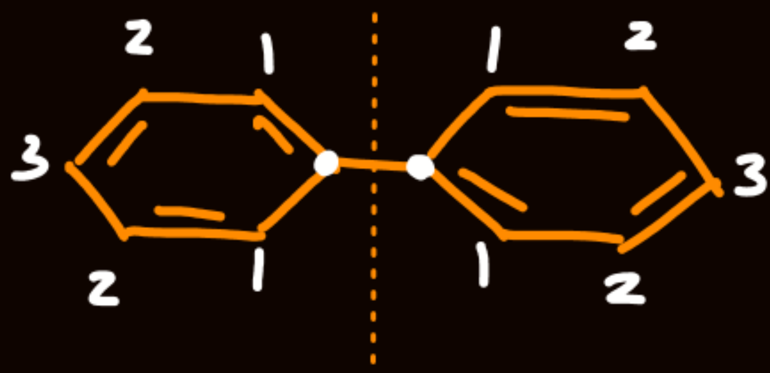
3 diff H
↓
3 Mcd

Que Diphenyl methane



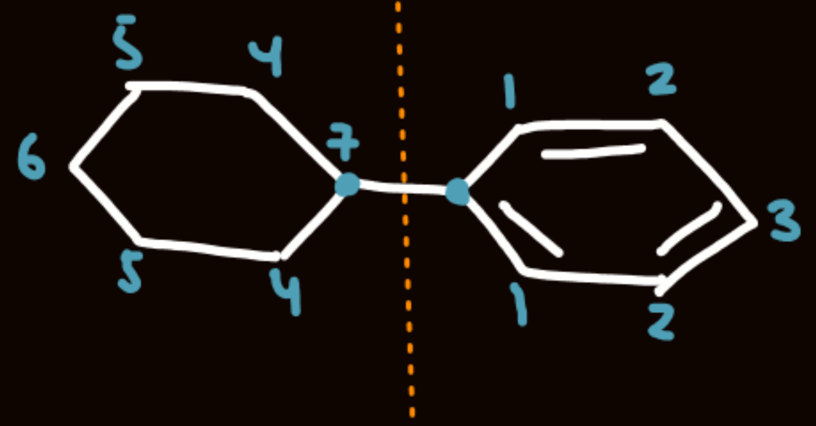
4 diff H
↓
4 Mcd

Que Biphenyl



3 diff H
↓
3 Mcd

Que Cyclohexyl Benzene



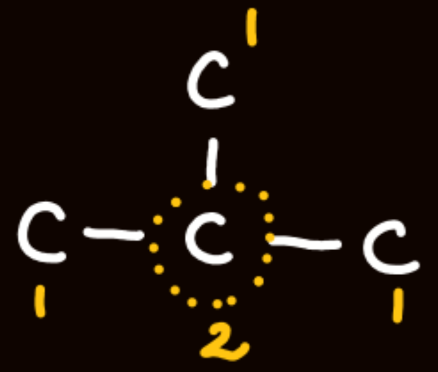
7 diff H
↓
7 Mcd

Que 3-methylpentane



4 diff H
↓
4 Mcd

Q Isobutane



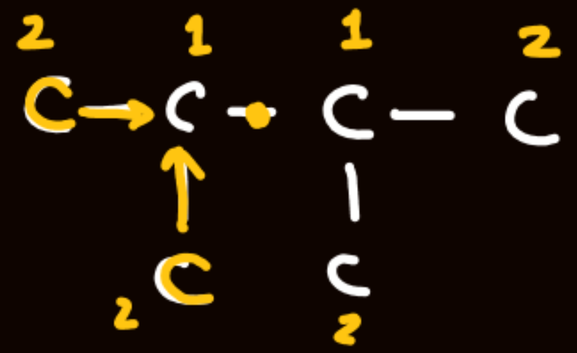
2 diff H → 2 mcd

Q neopentane



→ 1 diff H → 1 mcd

Q 2,3-dimethylbutane



2 diff H → 2 mcd

Stereoisomerism

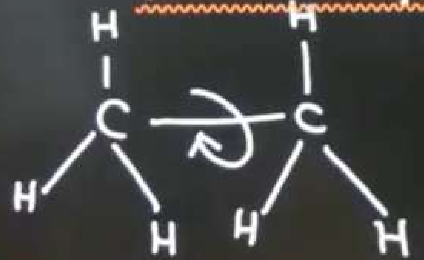
StereoIsomerism

- Same MF, Same structural formula, Same IUPAC
- Diff arrangement (angle of rotation) of atom in 3 dimension (spatial (↳3d) arrangement is diff)

StereoIsomerism

Conformational Isomerism	Configurational isomerism ✗

① Same MF, same str Formula
diff angle of rotation (arrangement)
of atom/group in space
around free rotation of Sigmabond (Singlebond)

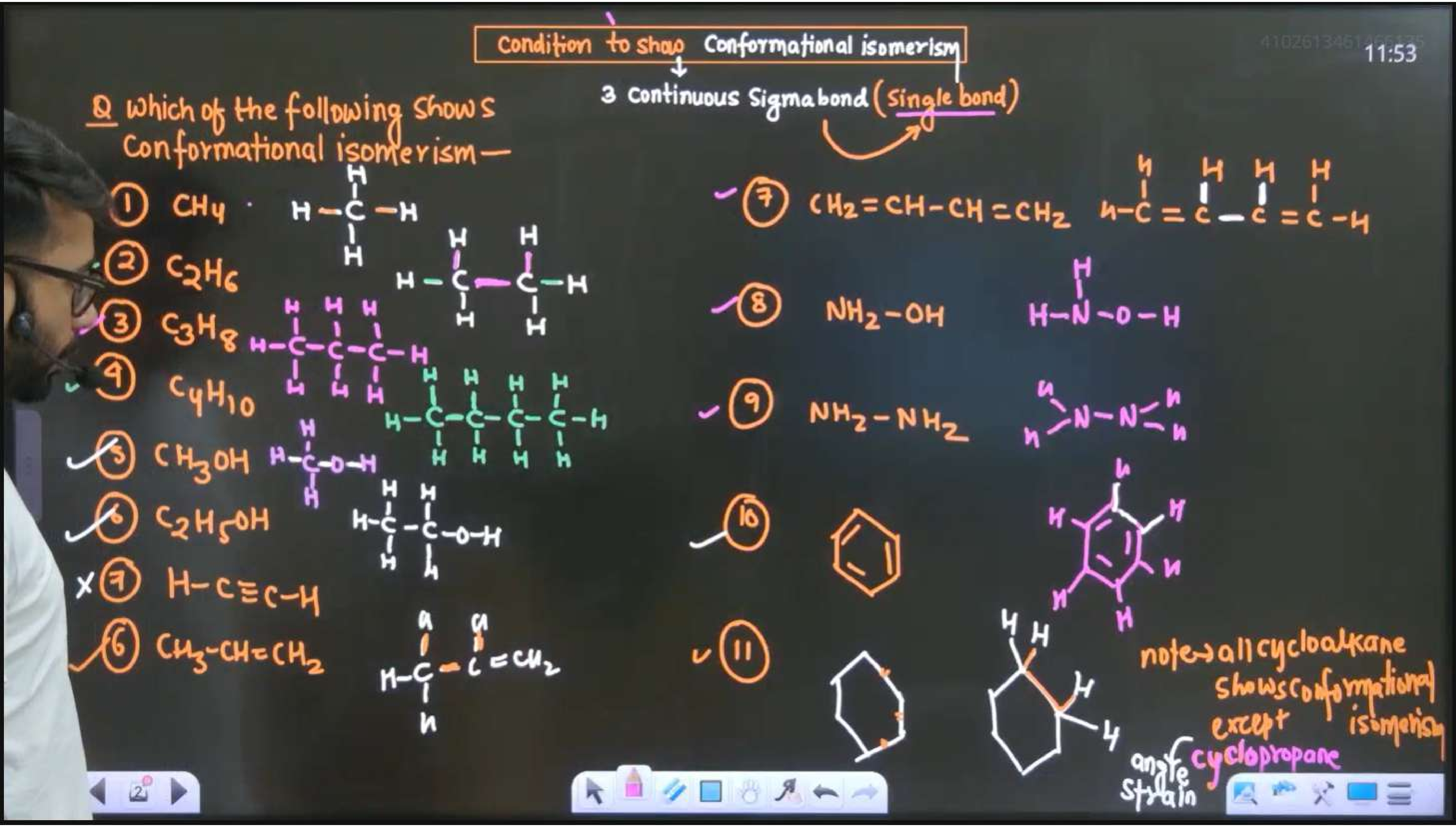


→ The energy req to rotate comp across Sigmabond is obtained from room temp.

② Rotational isomerism (Rotamers)

③ pseudo isomers (not true isomer) → Due to rapid & Continuous rotation across sigma bond it is impossible to separate two conformer. Therefore it is called Pseudoisomer.

- There are ∞ conformers of a molecule.



Condition to show Conformational isomerism
3 Continuous Sigma bond (single bond)
Q Which of the following shows Conformational isomerism—
① CH4
② C2H6
③ C3H8
④ C4H10
⑤ CH3OH
⑥ C2H5OH
⑦ H−C≡C−H
⑥ CH3−CH=CH2
⑦ CH2=CH−CH=CH2
⑧ NH2−OH
⑨ NH2−NH2
⑩
⑪
note → all cycloalkane shows conformational isomerism except cyclopropane
angle strain
11:53

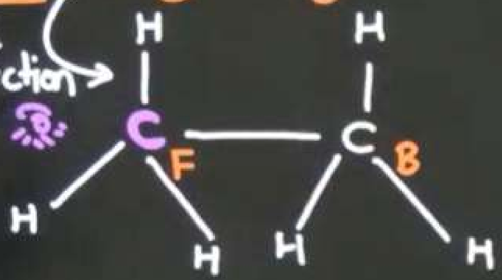
12:10

परछाई ← Projection of molecule

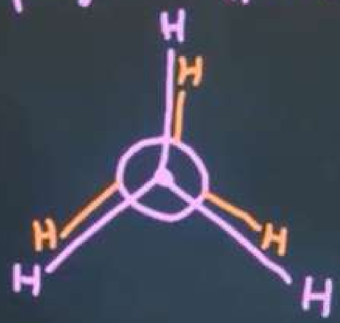
तु खींच मेरी photo

Que ethane $CH_3—CH_3$

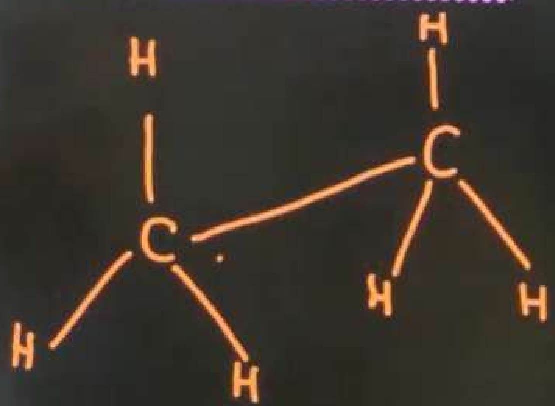
3d projection

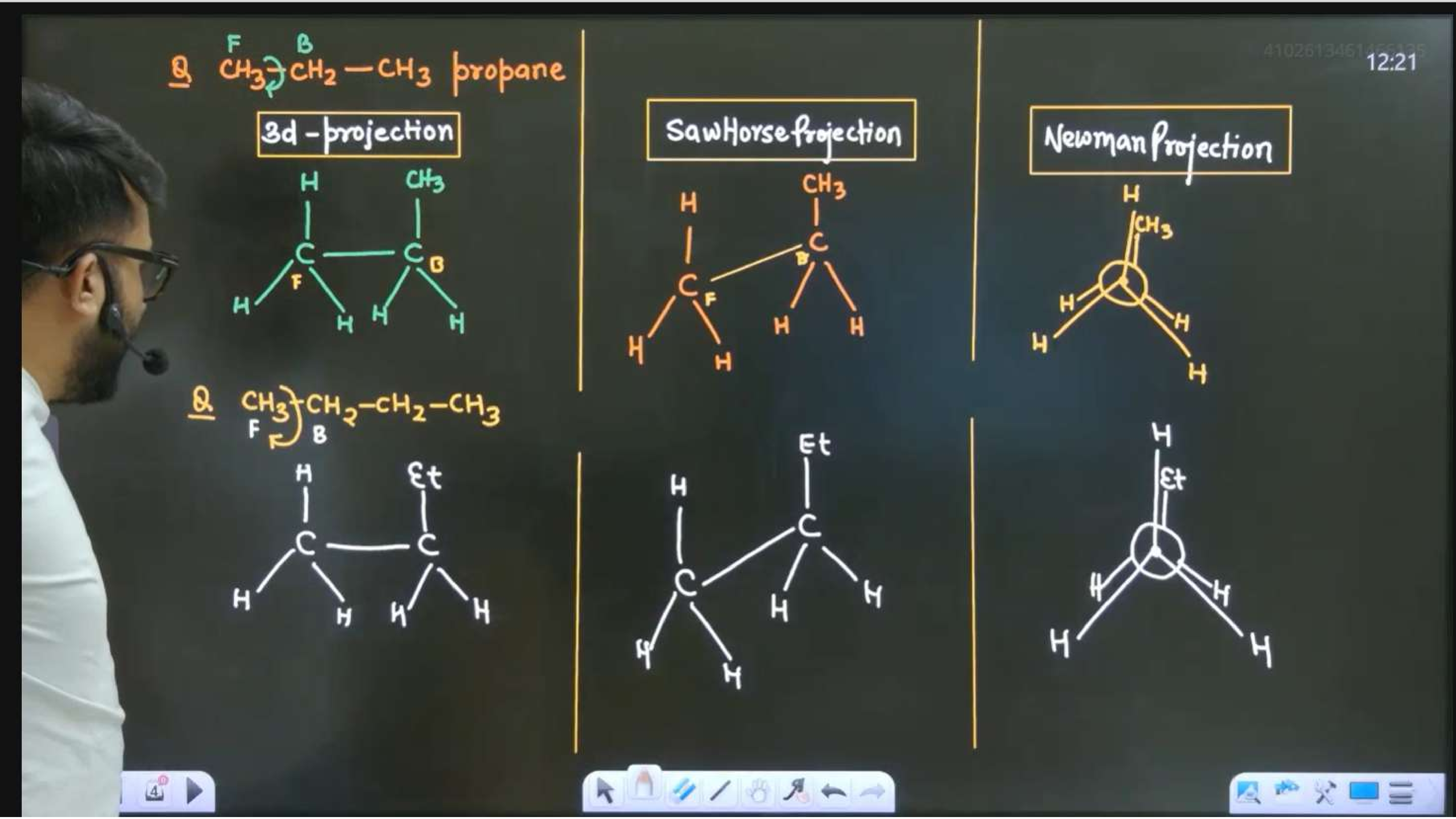


newman projection (front view)



Sawhorse projection (sideview)

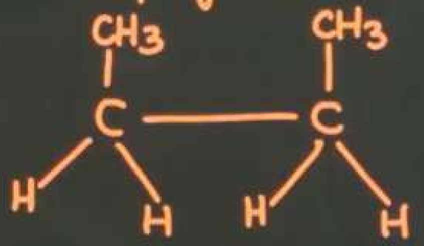




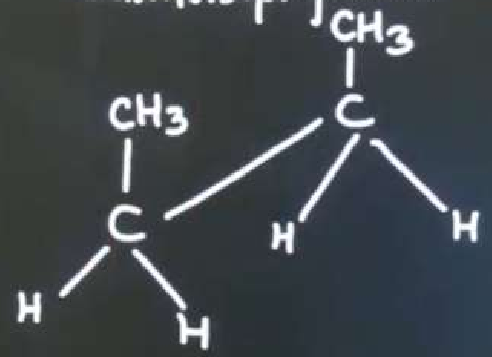
Q CH3–CH2–CH3 propane
3d-projection
SawHorse Projection
Newman Projection
Q CH3–CH2–CH2–CH3
12:21

Q $CH_3-CH_2-CH_2-CH_3$

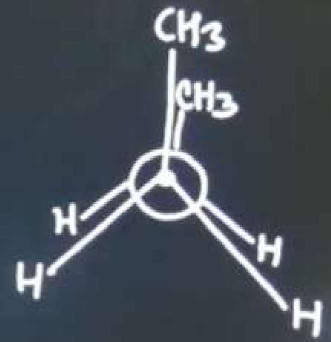
3d projection



Sawhorse projection



Newman projection



Some Imp definitions-

① **Steric strain / Vanderwall strain** → Repulsion b/w 2 bulky group in newman projection.

Strain ≡ Repulsion

$$\text{Steric strain / Vanderwall strain} \propto \text{Size} \propto \frac{1}{\text{distance}}$$

② **Tortional strain** → Repulsion b/w bond pair of electron in newman projection.

$$\text{Tortional strain} \propto \frac{1}{\text{distance}}$$

$$\text{Stability} \propto \frac{1}{\text{Strain}} \propto \frac{1}{\text{Energy}}$$

$$\text{Strain} \propto \text{Energy}$$

③ **Dihedral Angle** → ① Angle b/w 2 diff Plane

② Angle b/w 2 bulky group of different Carbon.

NOTE → During conformational isomerism bond angle, bond length do not change. only dihedral angle changes.

Que Min Carbon req in alkane to show Conformational isomer — 2

Que " " " Cycloalkane " " " — 4

Que " " " any organic comp " " " — 0

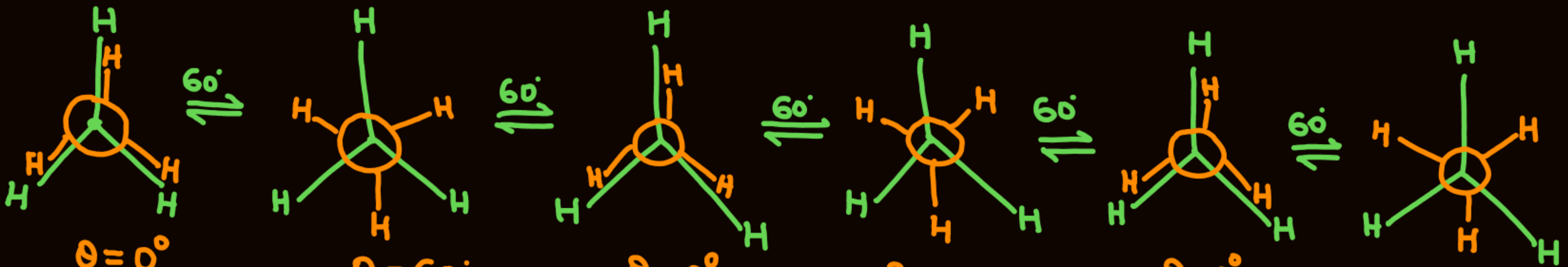
Conformational isomerism in ethane

$CH_3 \rightleftarrows CH_3$

F B

* max stable conformer → Staggred
* min " " → Eclipsed
* min stable → max stable → θ = 60°
* max stable → min stable → θ = 60°

min stable → min stable = θ 120°
max stable → max stable = θ 120°



① θ = 0°, Eclipsed, φ = 0°

② θ = 60°, Staggered, φ = 60°

③ θ = 0°, Eclipsed, φ = 120°

④ θ = 60°, Staggered, φ = 180°

⑤ θ = 0°, Eclipsed, φ = 240°

⑥ θ = 60°, Staggered, φ = 300°, 1 V60°



⑦ θ = 0°, Eclipsed, φ = 360°

Stab ∝ $\frac{1}{PE}$

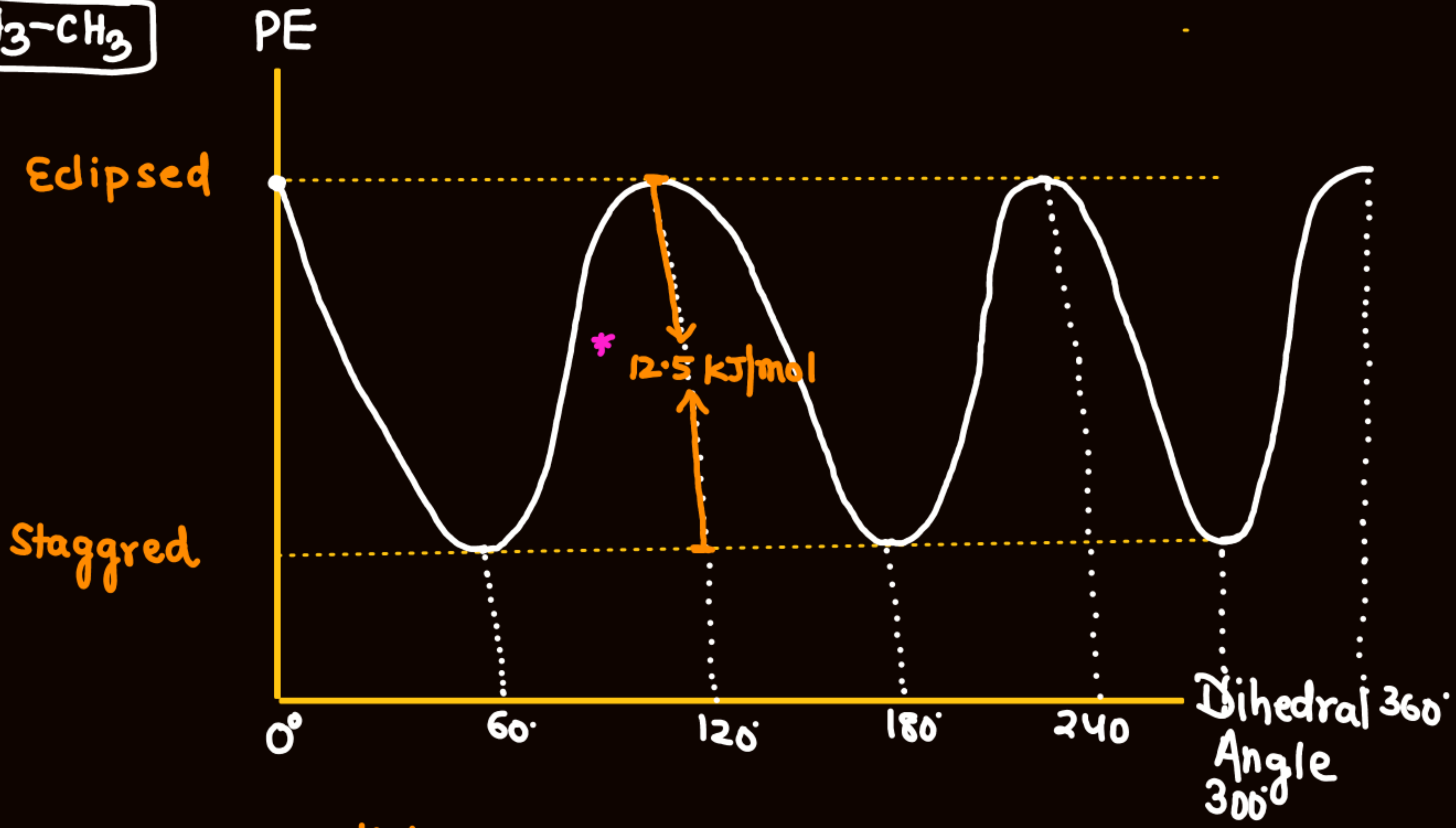
Stability → Staggred > eclipsed

2 = 4 = 6 > 1 = 3 = 5 = 7

Potential Energy → Staggered < Eclipsed

2 = 4 = 6 < 1 = 3 = 5 = 7

CH_3-CH_3



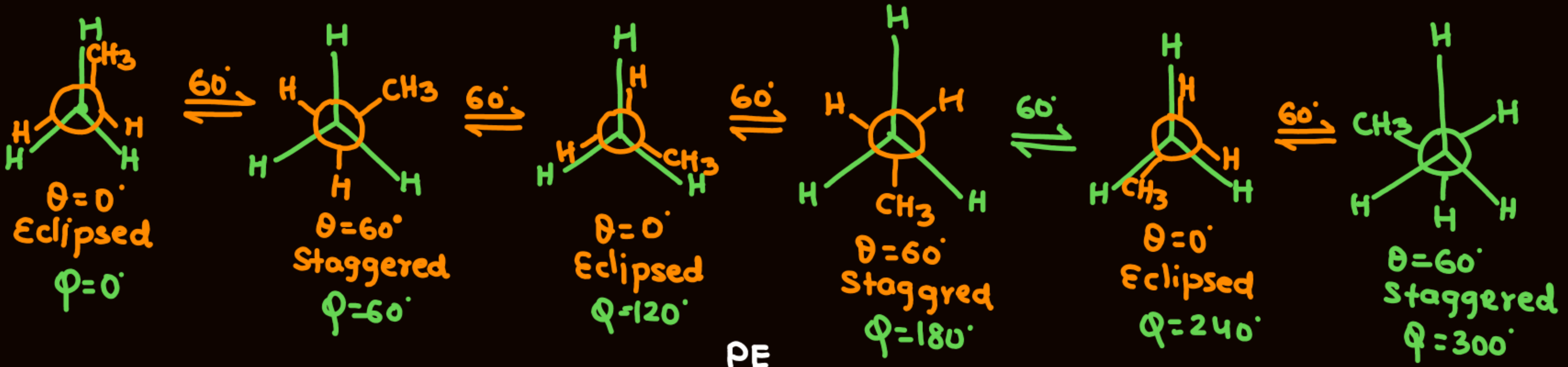
Highest Energy − Lowest Energy = 12·5 KJ/mol

Eclipsed En − Staggred En = 12·5 KJ/mol

* For any alkane the energy gap b/w lowest & Highest is 1-21 KJ/mol

Conformational isomerism of Propane

$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_3$ (F, B)
↳ across C_1-C_2

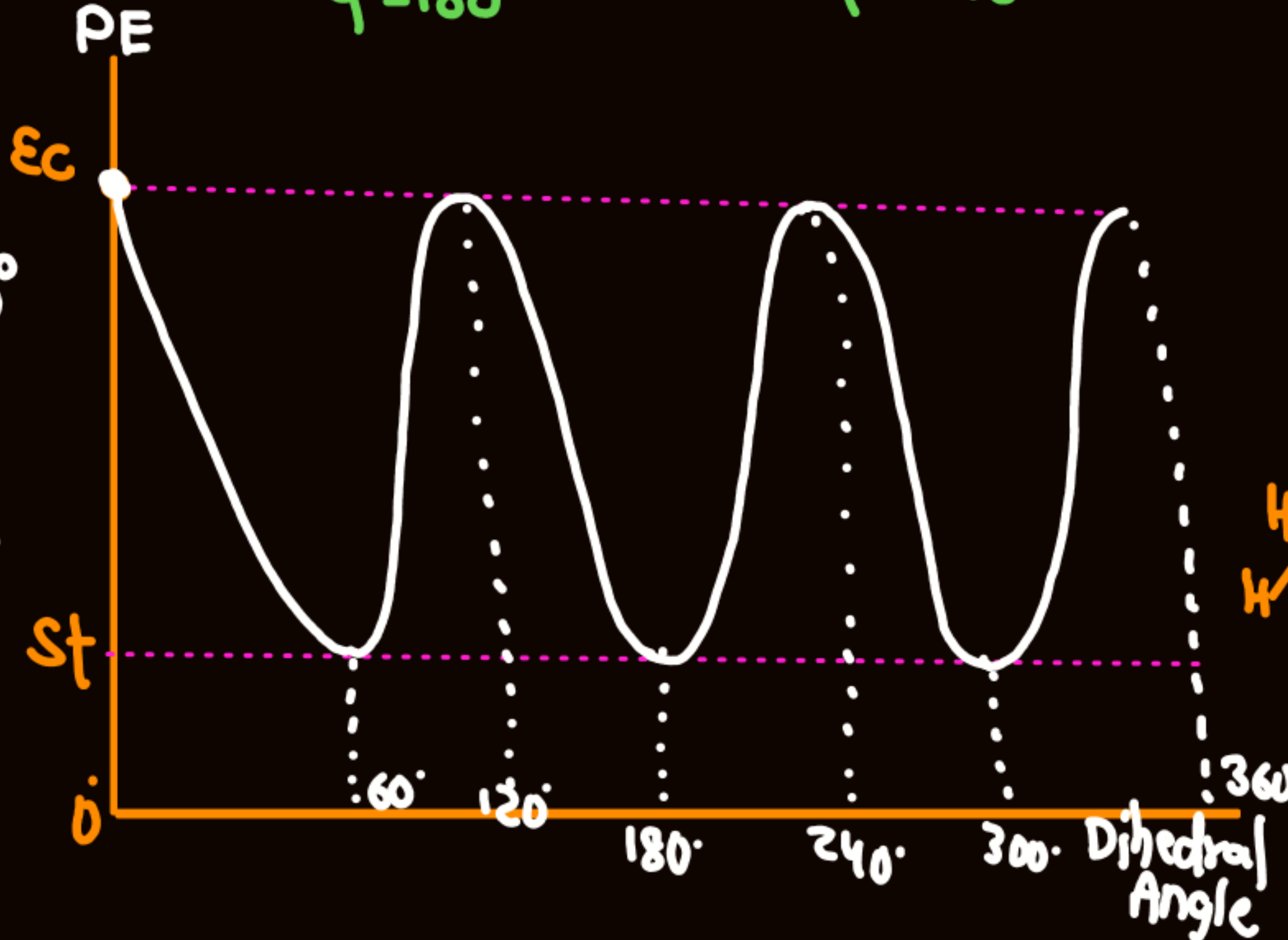




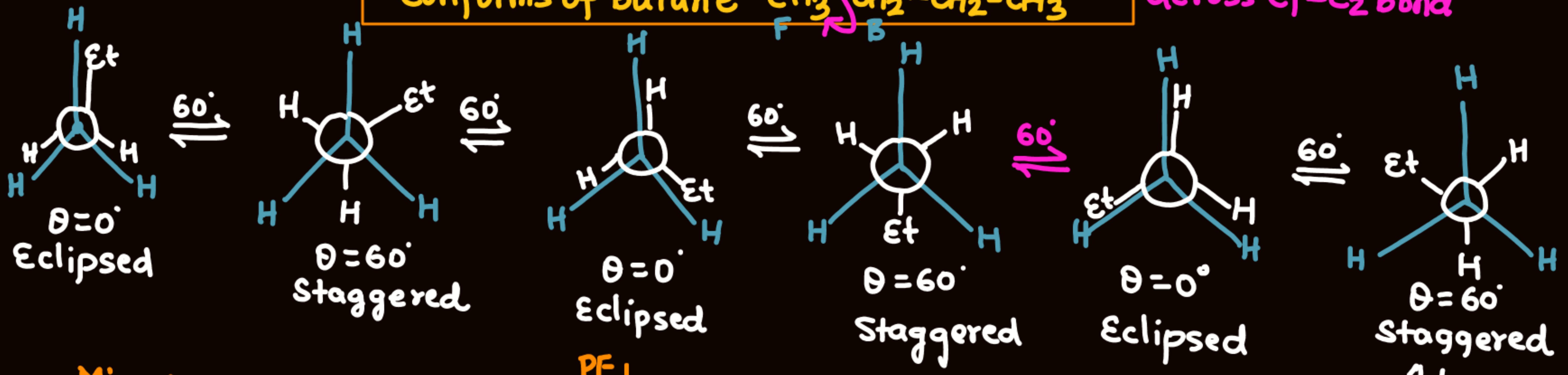
max stable → Staggred
min stable → Eclipsed
minstable → maxstable θ = 60°
maxstable → min stable θ=60°
min stable → min Stable = θ = 120°
maxstable → maxstable = θ = 120°

Stability → Staggered > Eclipsed
→ 2=4=6 > 1=3=5=7

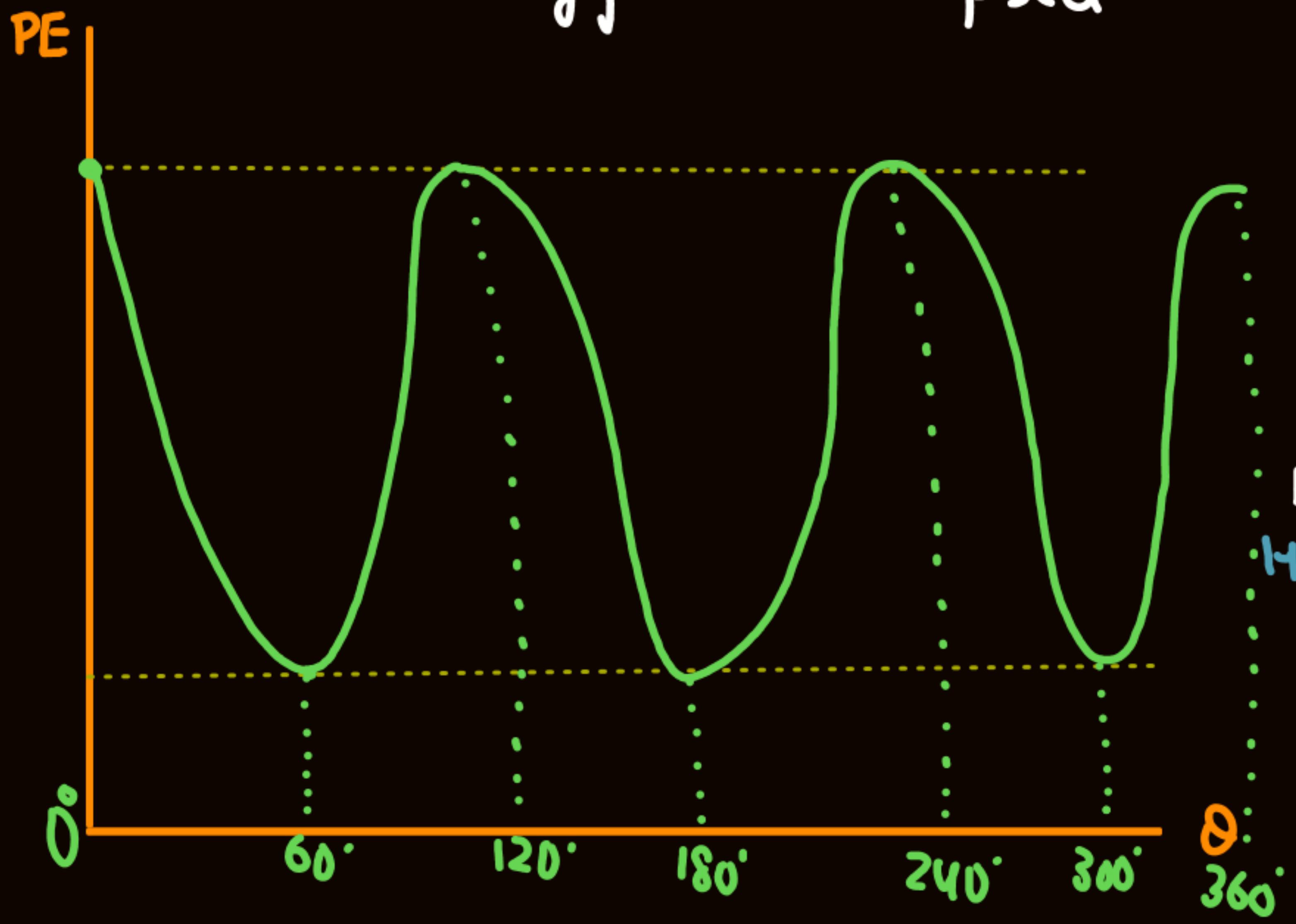
PE → Staggred < Eclipsed
→ 2=4=6 < 1=3=5=7

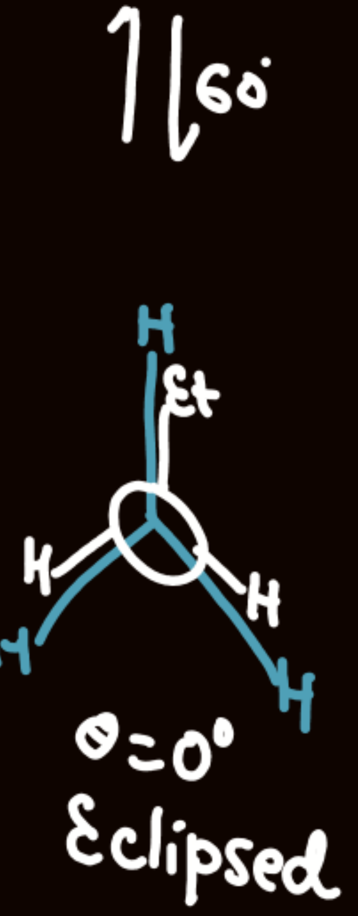


Conforms of Butane $\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$ across C_1-C_2 bond

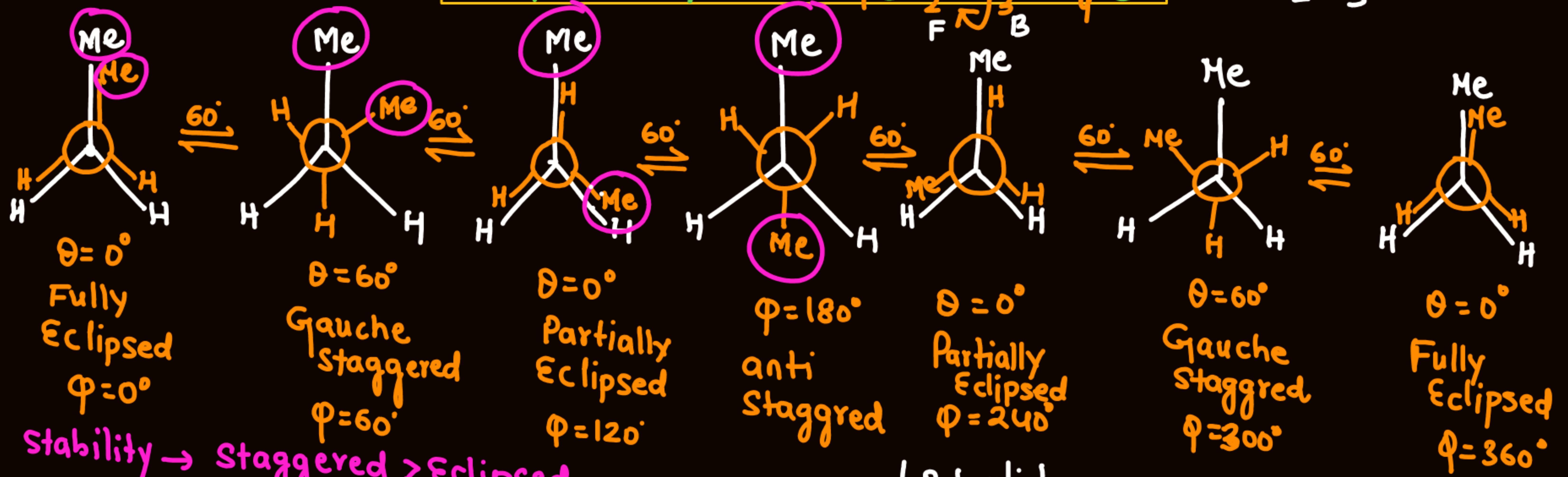


Min stable → Eclipsed
Max stable → Staggered
Min stable → Max stable θ=60°
Max stable → Min stable = θ=60°
Min stable → Min stable = θ=120°
Max stable → Max stable = θ=120°
Stability → Staggered > Eclipsed
→ 2=4=6 > 1=3=5=7
PE → Staggered < Eclipsed
2=4=6 < 1=3=5=7





Conformer of butane $CH_3-CH_2-CH_2-CH_3$ across C_2-C_3



Stability → Staggered > Eclipsed

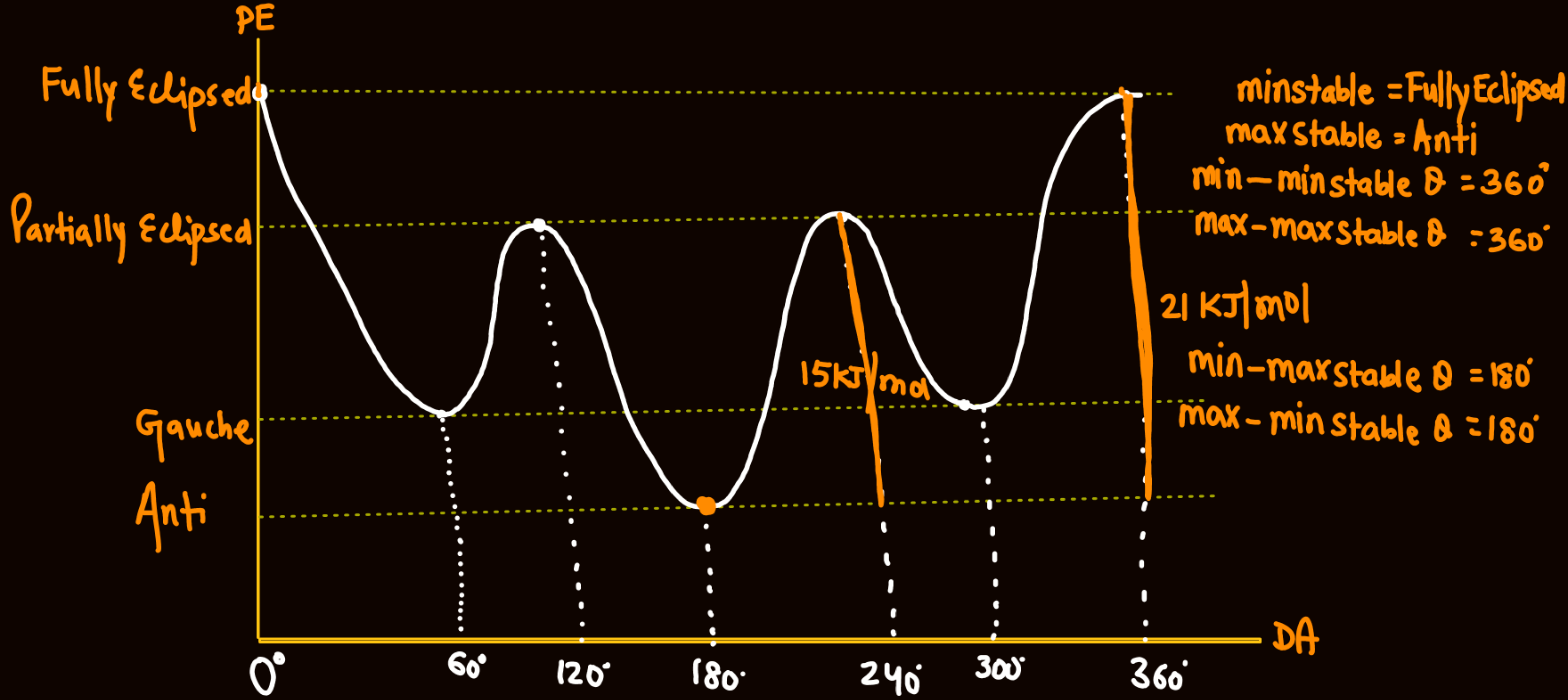
Anti Staggred > Gauche Staggered > Partially eclipsed > Fully Eclipsed

④ > 2 = 6 > 3 = 5 > 1 = 7

Potential Energy → Staggred < Eclipsed

Anti Staggred < Gauche Staggred < Partially Eclipsed < Fully Eclipsed

4 < 2 = 6 < 3 = 5 < 1 = 7



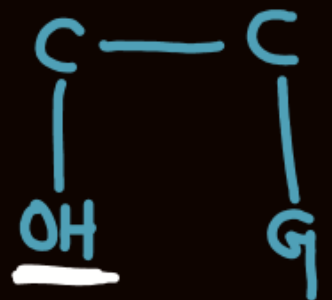
Stab → Anti > Gauche > Partially eclipsed > Fully Eclipsed

Questions on stability order of Conformers

Generally → Anti ($\theta = 180°$) is more stable than Gauche ($\theta = 60°$).

But → in some cases Gauche is more stable than Anti.

1. Intramolecular Hydrogen Bonding → Syllabus
2. Ionic attraction (attrn b/w charge) ✓
3. dipole-dipole attraction



G = OH | F | NO_2 | NH_2 | CHO | COOH | NO

N/O/F — $\overset{\delta+}{H}$ ...... F/O/N → HBonding

HBonding

N/O/F — $\overset{\delta+}{H}$ .... F/O/N/Cl

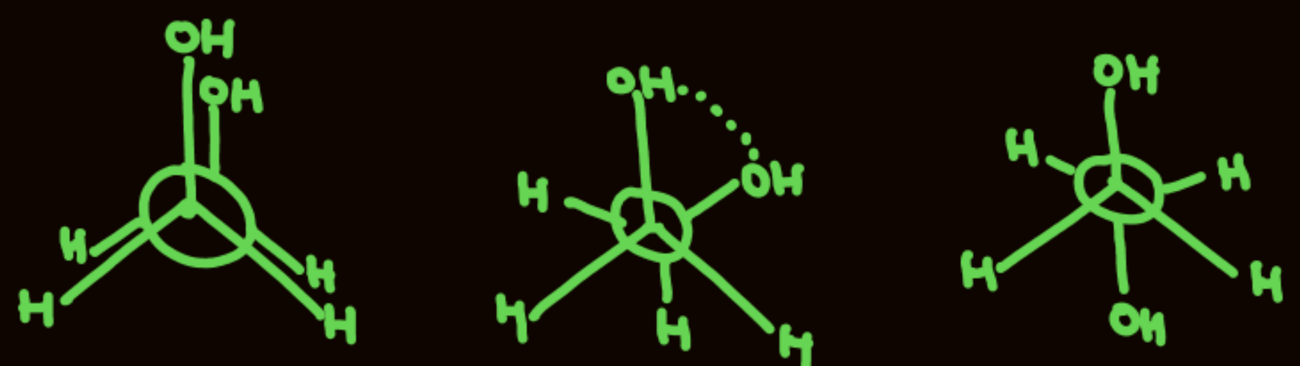
फीन कल

→ Gauche > Anti } stability

F — B

$CH_2(OH)-CH_2(OH)$ (OH ······ OH)

Stability → G > A
↓
H Bond



Eclipsed

TS ✓

SS / VS ✓
↓
Unstable

H Bond
↓
attrn
↓
En release
↓
Stable

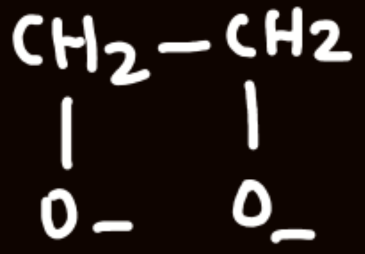
anti

NO_2

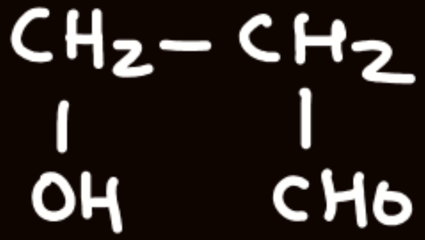
H–C=O

Gauche > Anti

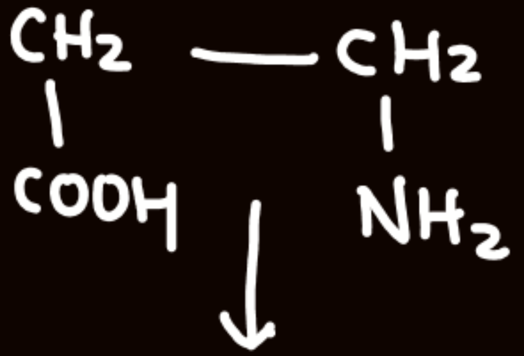
$CH_2(OH)-CH_2(OH)$ G>A	$CH_2(OH)-CH_2(NH_2)$ G>A	$CH_2(F)-CH_2(COOH)$ G>A	$CH_2(NO)-CH_2(F)$ A>G
$CH_2(OH)-CH_2(F)$ G>A	$CH_2(OH)-CH_2(NO_2)$ G>A	$CH_2(NH_2)-CH_2(COOH)$ G>A	$CH_2(COOH)-CH_2(NH_2)$ G>A
$CH_2(OH)-CH_2(O^-)$ G>A	$CH_2(OH)-CH_2(NO)$ G>A	$CH_2(NO_2)-CH_2(CHO)$ A>G	$CH_2(F)-CH_2(F)$ A>G



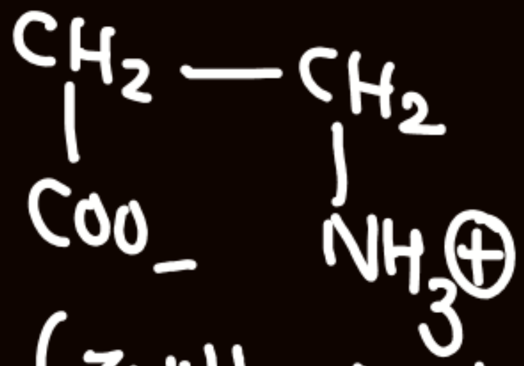
A > G



G > A



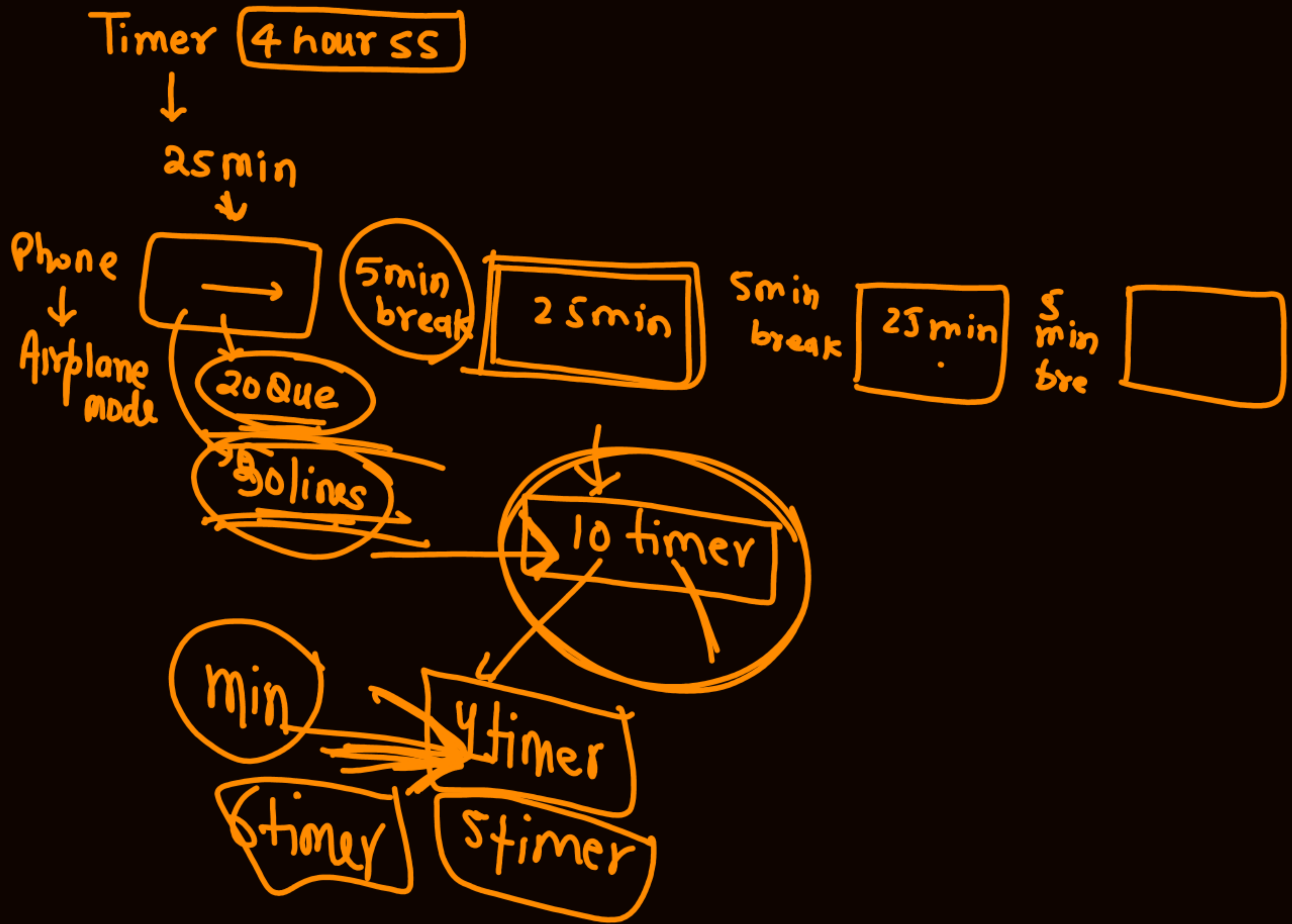
→ G > A



→ G > A

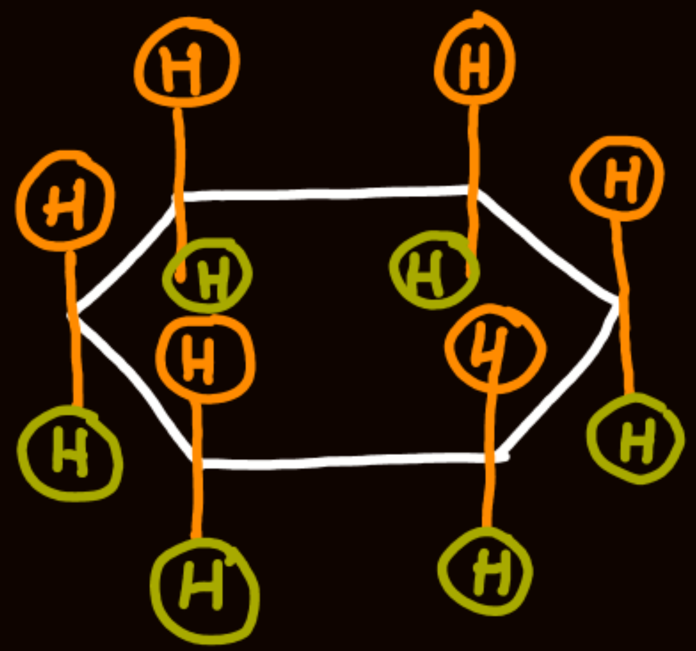
(zwitter ion)

Challange#1



Timer
4 hour ss
25min
Phone
Airplane mode
5min break
25min
5min break
25min
5 min bre
20Que
90lines
10 timer
min
4timer
5timer
5timer

Conformational isomerism in cyclohexane



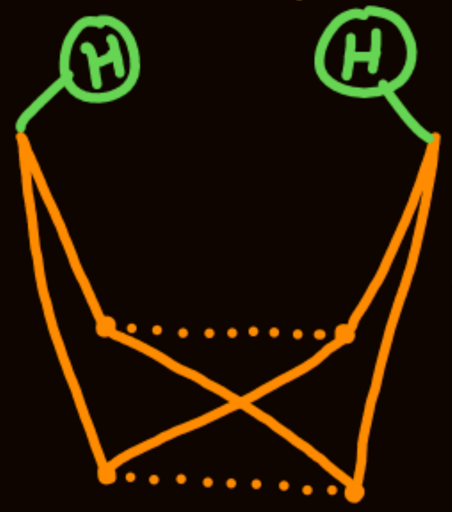
Cyclohexane
↓
12H eclipsing
↓
Repulsion
↓
Unstable

⇌



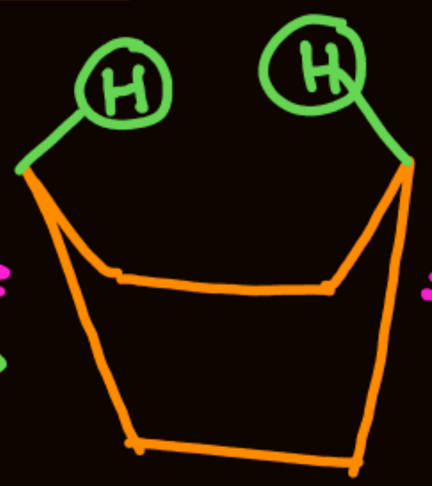
Chair Form
↓
Repulsion is min
↓
Stable

⇌ >



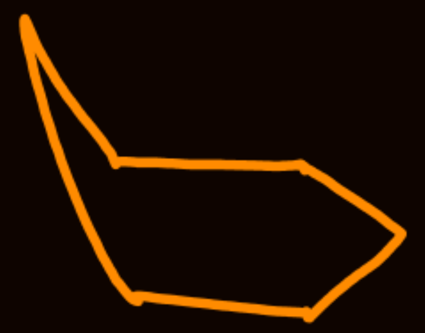
Twist boat
↓
FlagPole Hydrogen Repulsion is less

⇌ >



Boat form
↓
FlagPole Hydrogen Repulsion is more

⇌ >

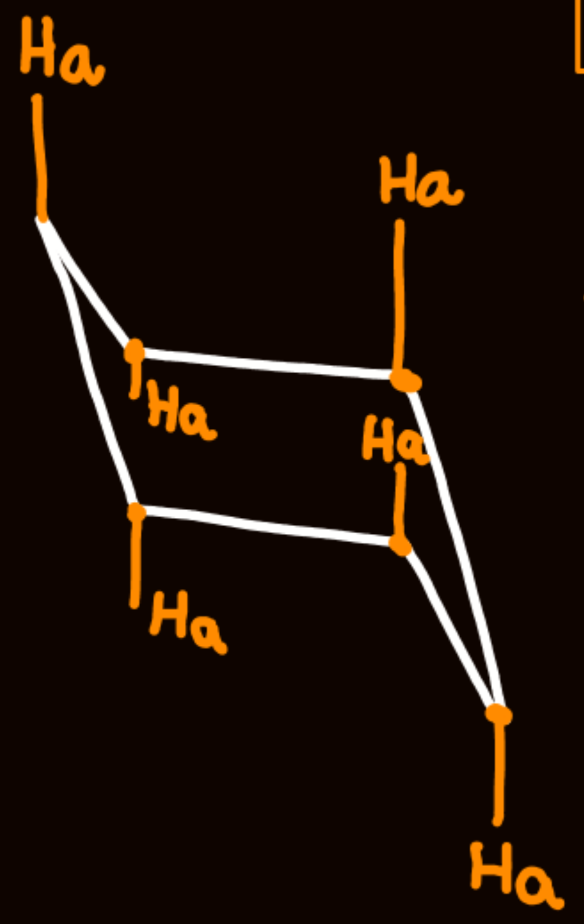


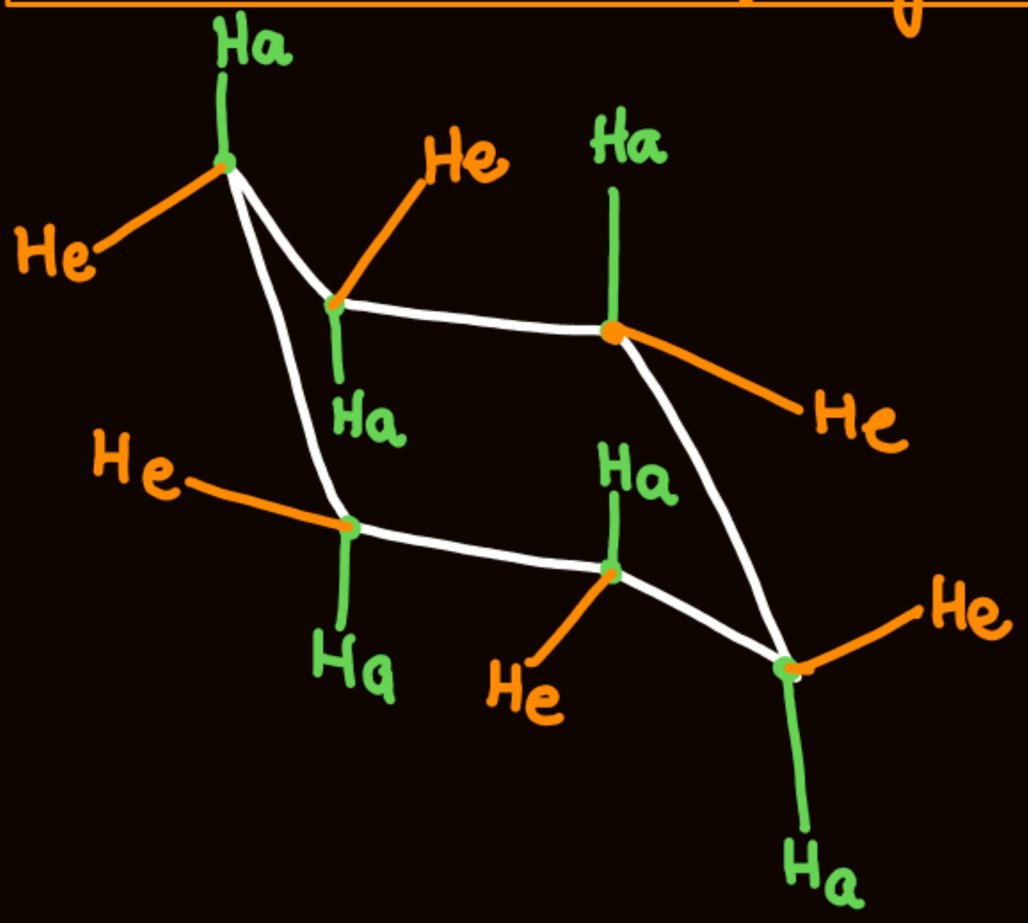
↓
Half Chair
↓
Repulsion is max
↓
Unstable

Stability → Chair > Twist boat > boat > Half chair

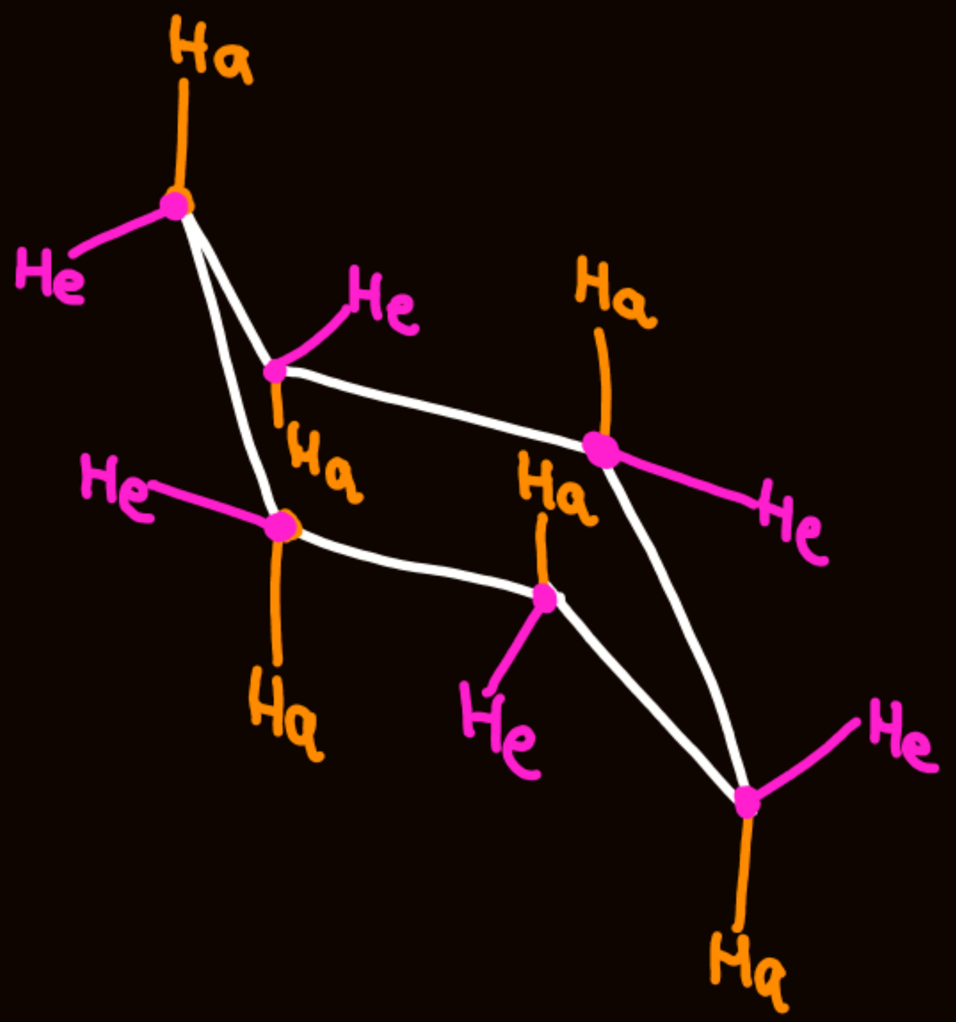
→ class Test Bhi Hai

Axial & Equitorial Hydrogen in chair Form

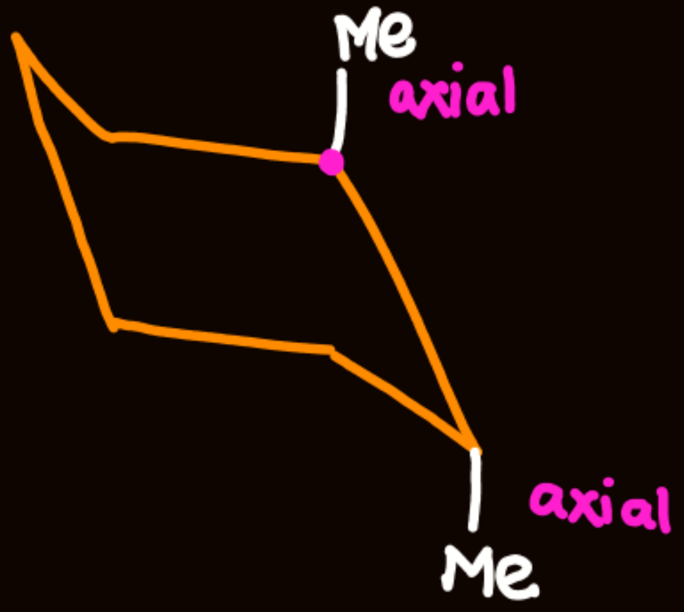




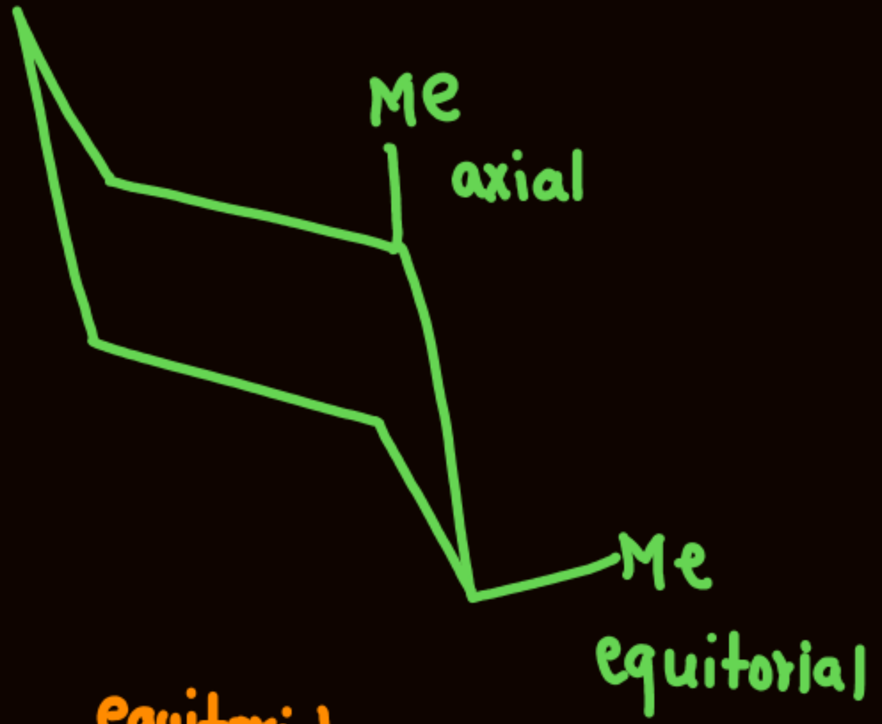
12 H
↓
6 axial H → Ha } alternate up & down.
6 equitorial H → He } alternate up & down
↓



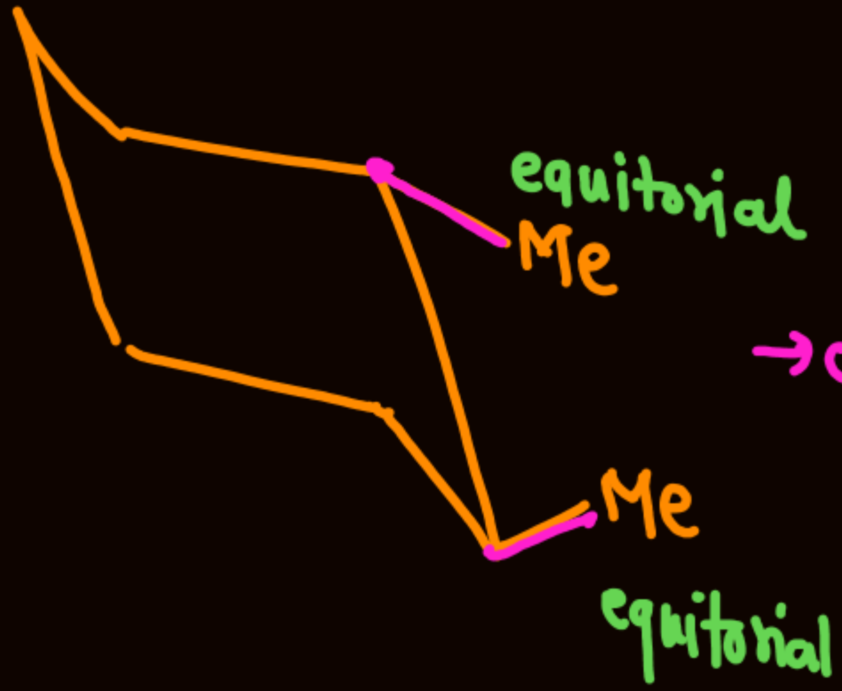
Stability in chair Form



→ Cys



→ Trans

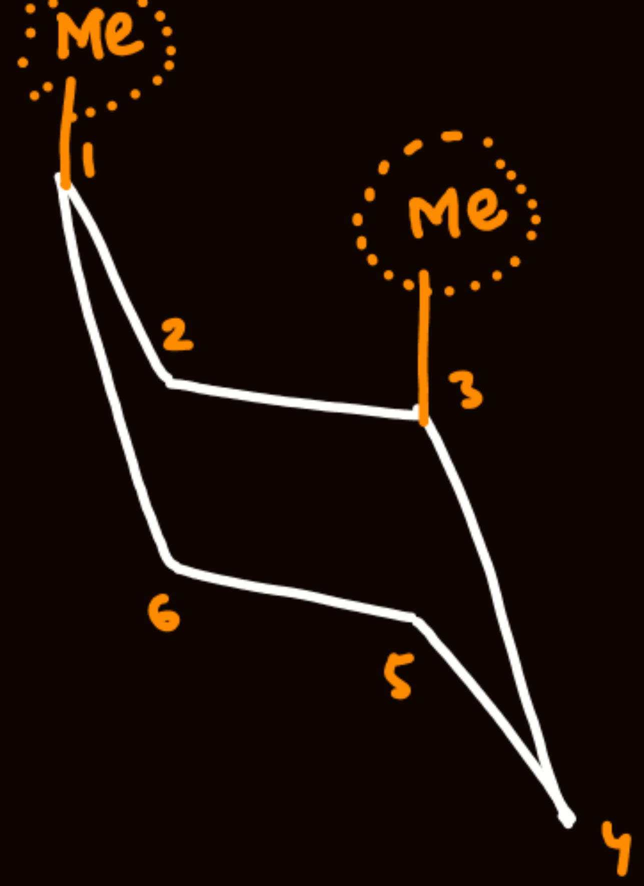


→ Cys



→ Trans

Stability order In chair Form

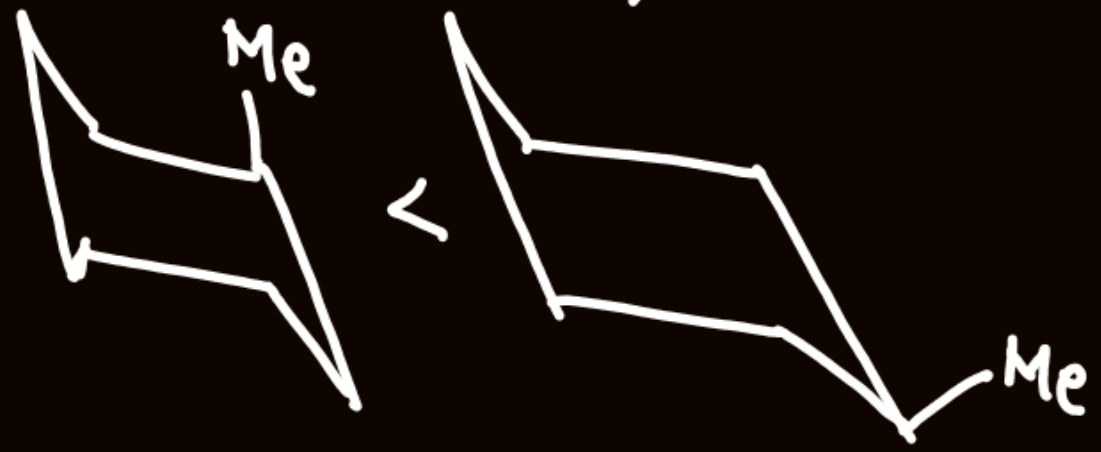


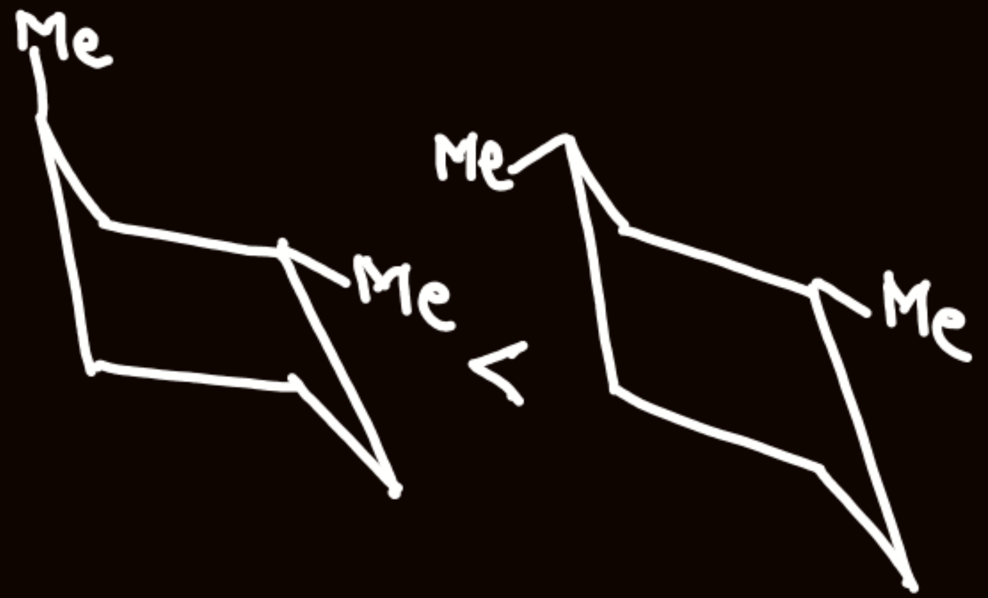
→ Bulky group on axial position → Repulsion → Unstable
↓
1,3-diaxial Repulsion

Bulky Group → equitorial position
↓
less Repulsion
↓
Stable

More bulky group on equitorial position is more stable

Que Compare stability







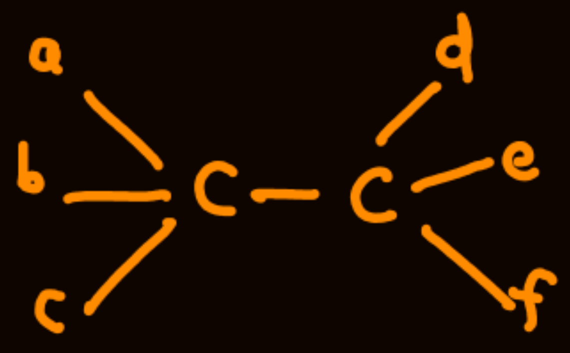
Configurational Isomerism

These isomers can not be converted into each other at room temp. around single bond. Hence they are two different compounds. These are k/a configuration isomers. (True Isomers)

Geometrical Isomerism

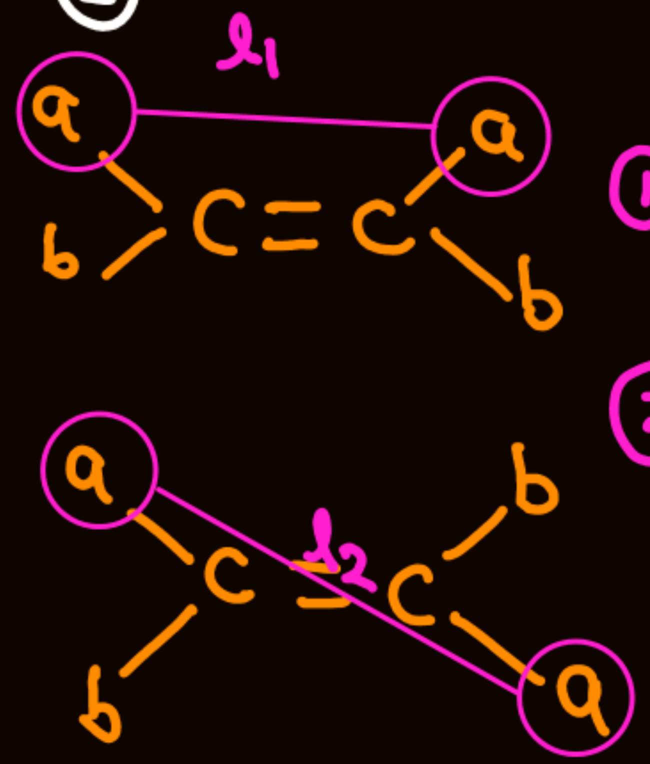
Two or more compound having diff arrangement of atom about Restricted Rotation System shows Geometrical isomerism.

①



Free Rotation
↓
GI ✗

②



① Restricted Rotation ✓

② $l_1 \neq l_2$ aerial distance is different

Condition to show GI

① Restricted Rotation

② aerial distance → different ($l_1 \neq l_2$)

Eg 3

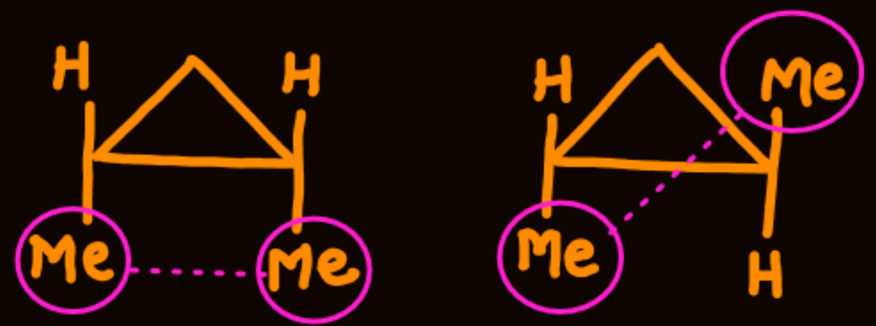
$Me-C\equiv C-Me$

1. Restricted Rotation ✓
2. aerial distance → same

⇓

Triple bond never shows GI

Eg 4



1. Restricted Rotⁿ ✓
2. aerial dist → diff

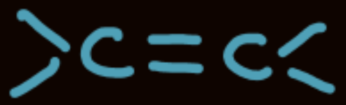
$l_1 \neq l_2$

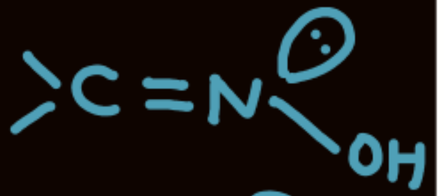
↓

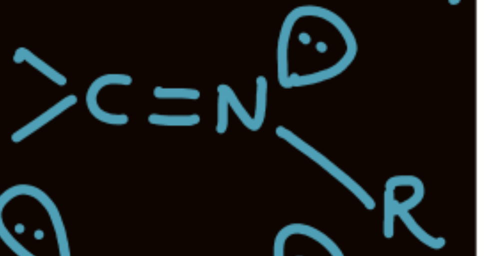
Shows GI

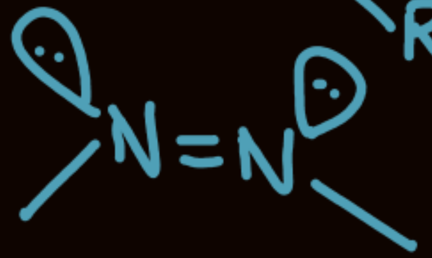
Restricted Rotation System

double bond

① alkene 

② oxime 

③ Imine 

④ Azo 

Ring

⑤ Cycloalkane

⑥ Cycloalkene

Special System

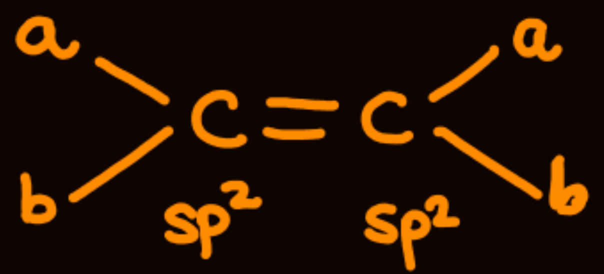
(DI)

⑦ Cummene

⑧ Biphenyl

⑨ Spiro Comp

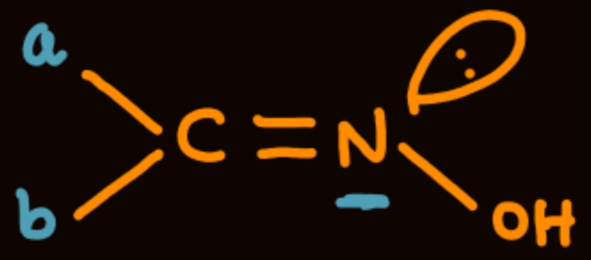
GI in alkene



① RR ✓

② Each sp^2 carbon should have diff bonded atom/group

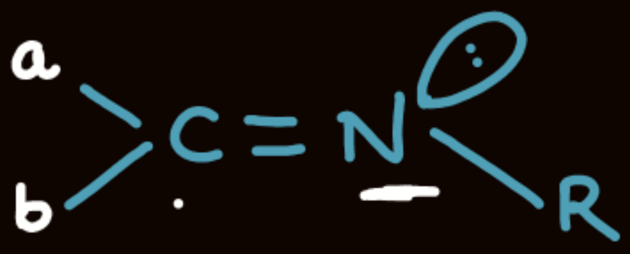
GI in oxime



① RR ✓

② sp^2 carbon should have diff bonded atom.

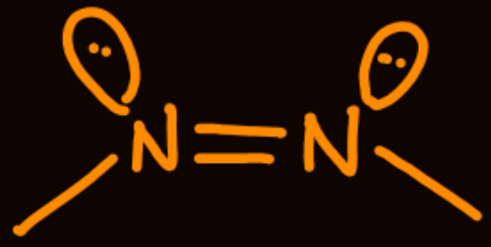
GI in Imine



① RR ✓

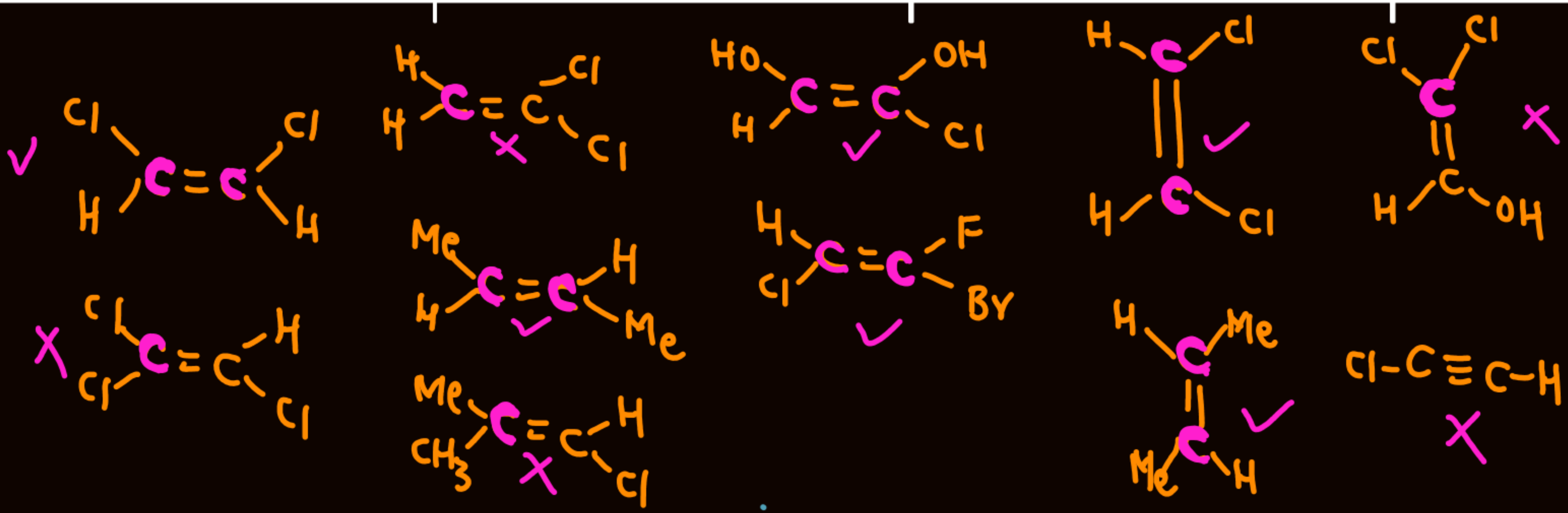
② sp^2 carbon should have different bonded atom

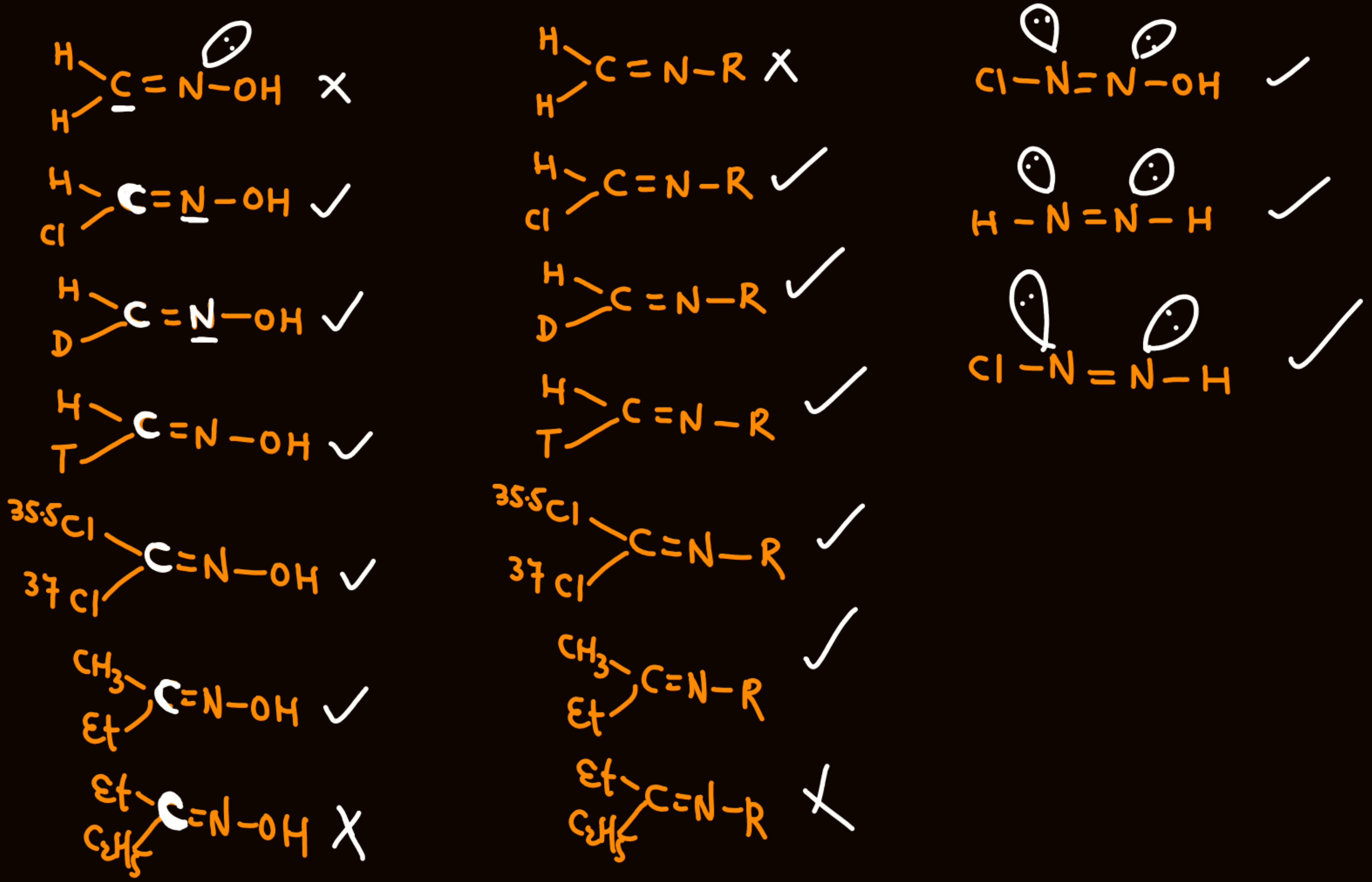
GI in azo



↓

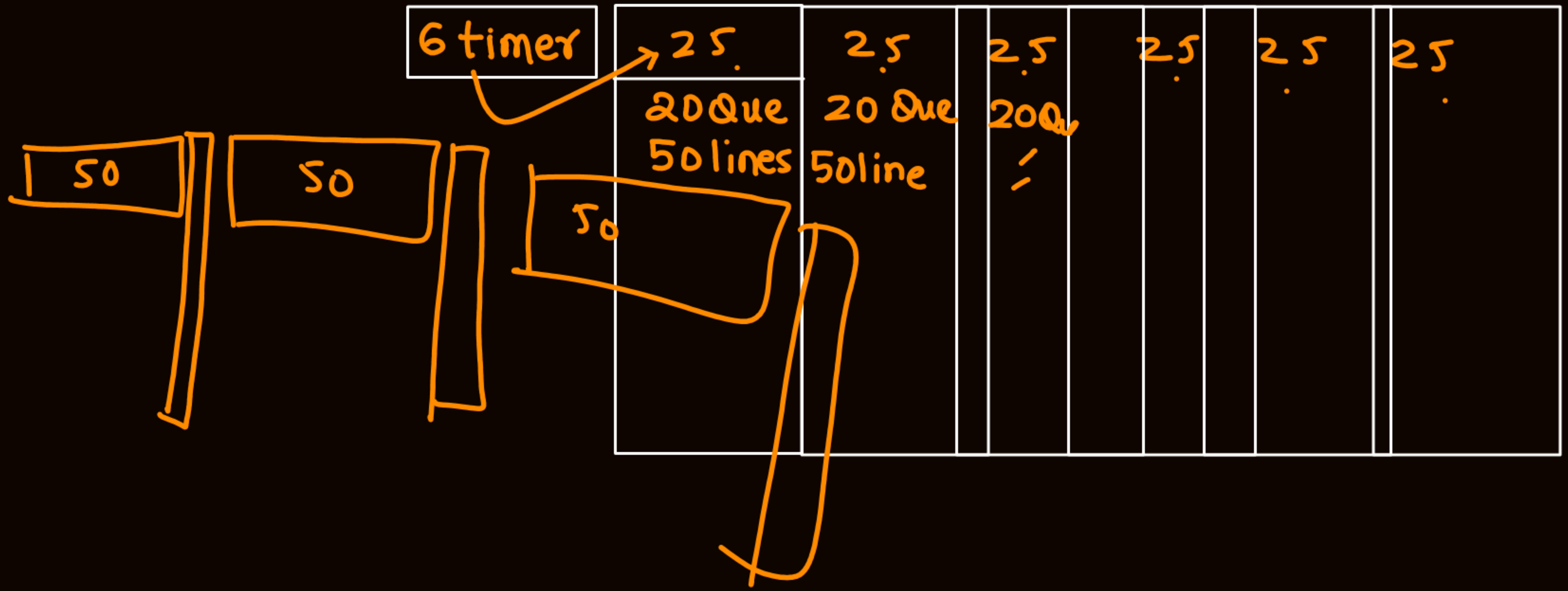
all azo compound show GI.





Challange#2

No Internet Challange



Today's Topic

1. Geometrical isomerism
   1. cycloalkane
   2. cycloalkene
2. Cys-Trans Configuration
3. E-Z configuration

Geometrical Isomerism

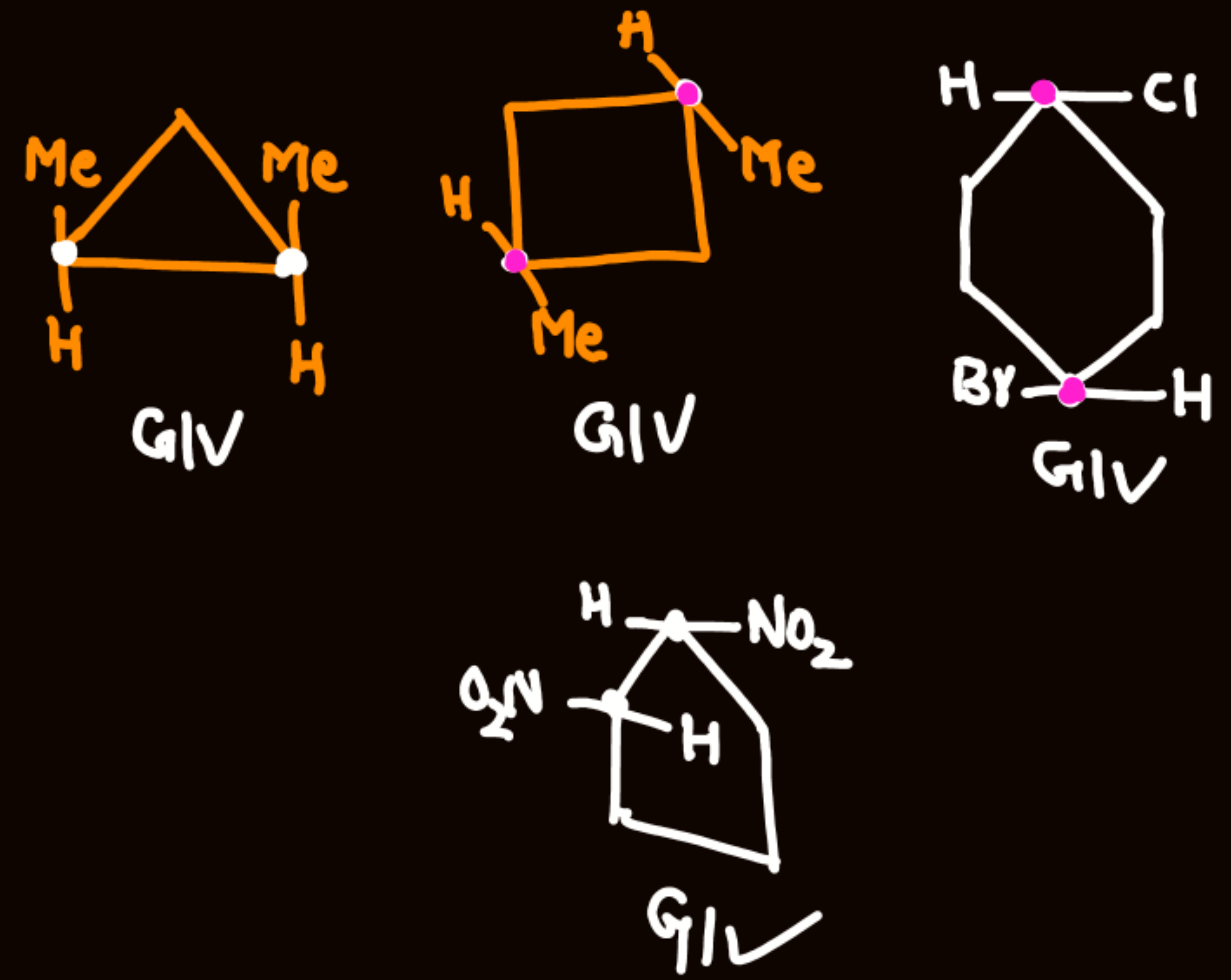
1. Restricted Rotation
2. aerial distance → diff
3. diff atom/group attached to both side of RR.

GI in Ring

Cycloalkane

① Restricted Rotation is present ✓

② diff atom/group attatched to any two sp^3 center. ✓



Cycloalkene

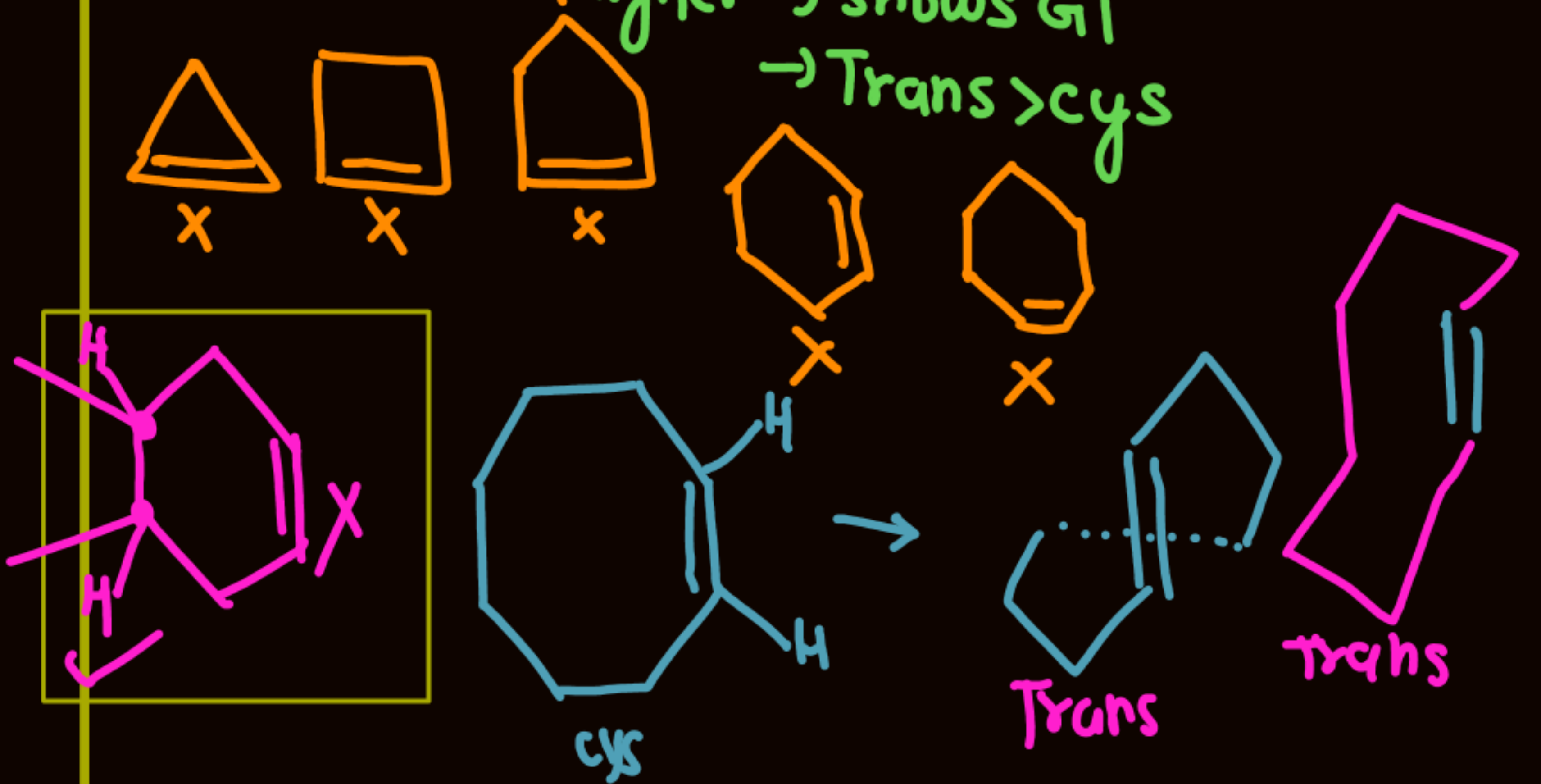
Case1 → GI possible bcoz of Ring → किसी भी दो sp^3 center पर diff atom/group attach हो तो GI Show होगा

Case 2 → GI possible bcoz of double bond

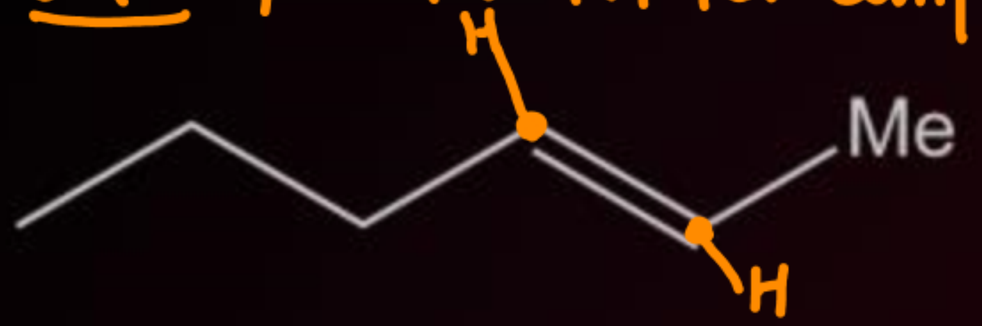
① 3 to 7 member Ring → donot show GI → bcoz of anglestrain

② 8 to 11 member Ring → shows GI
→ Cis > Trans → anglestrain is strain

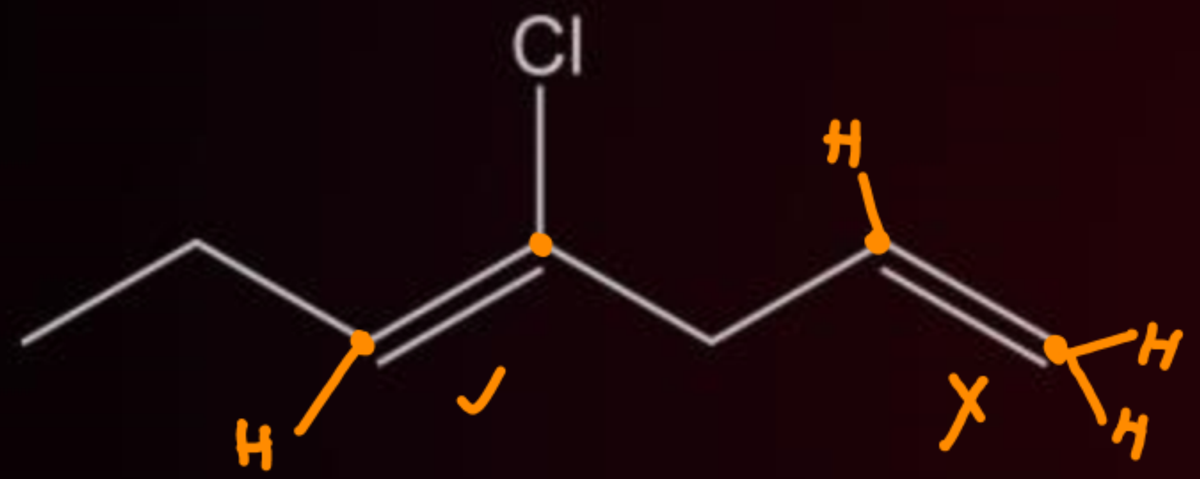
③ 12 member or higher → shows GI
→ Trans > cys



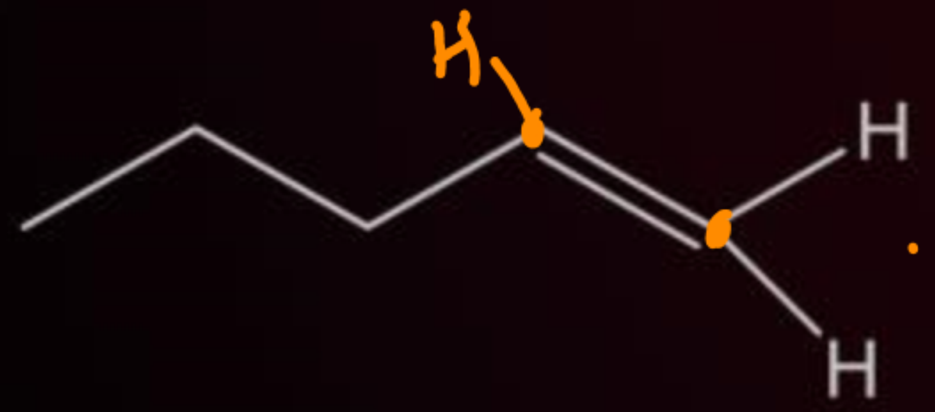
Que Find whether comp shows GI or not ??



✓

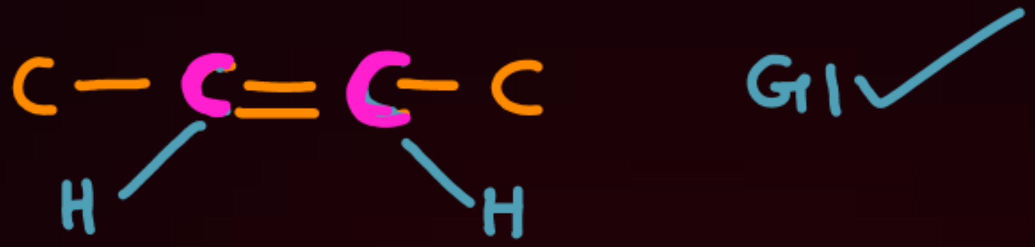


✓

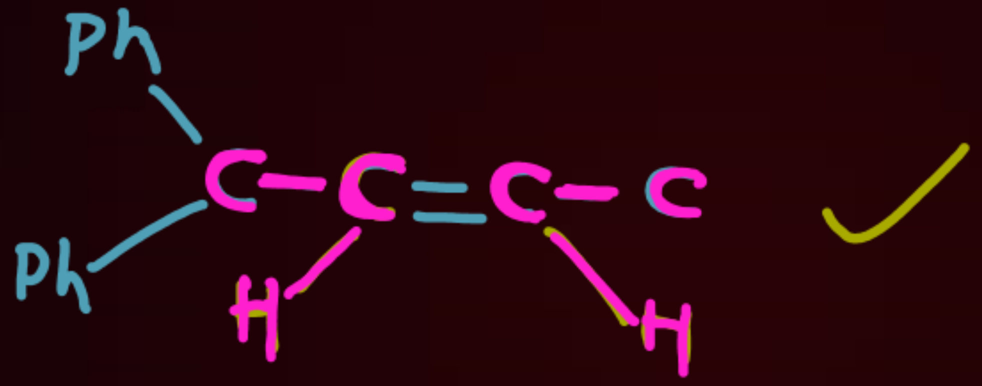


✗

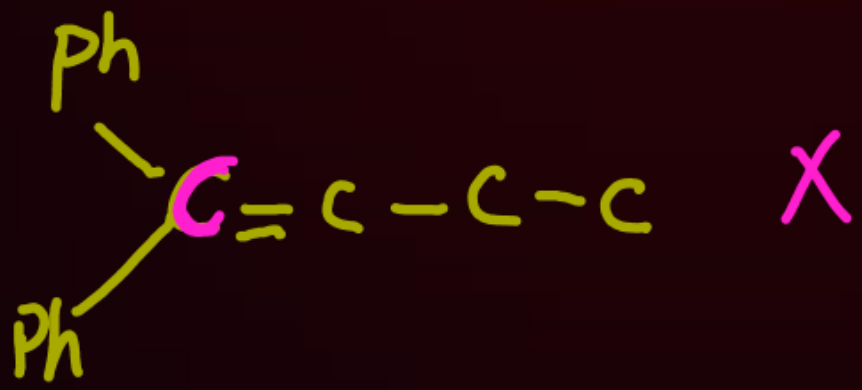
2 butene

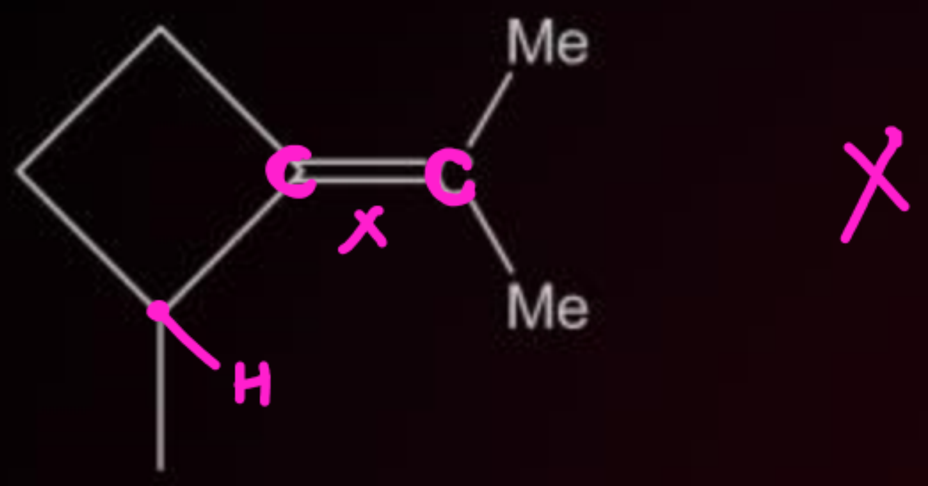


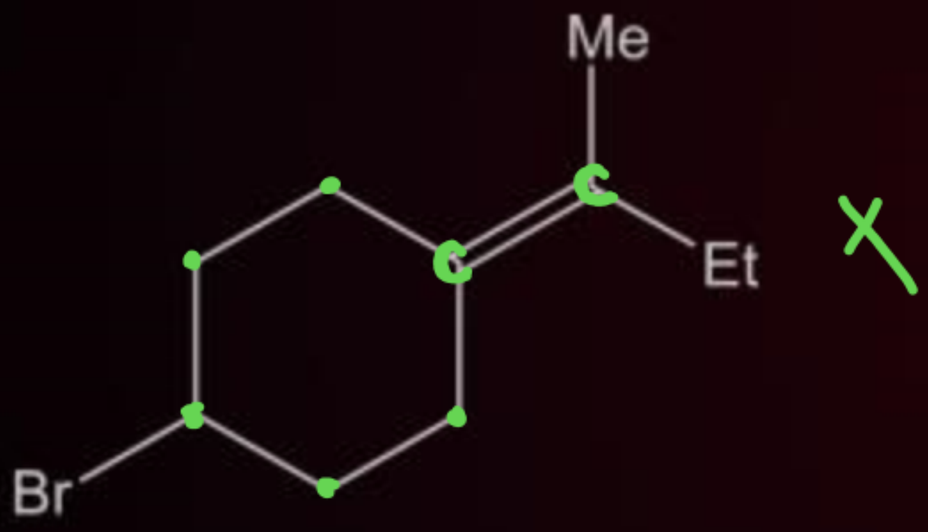
1,1-diphenyl-2-butene

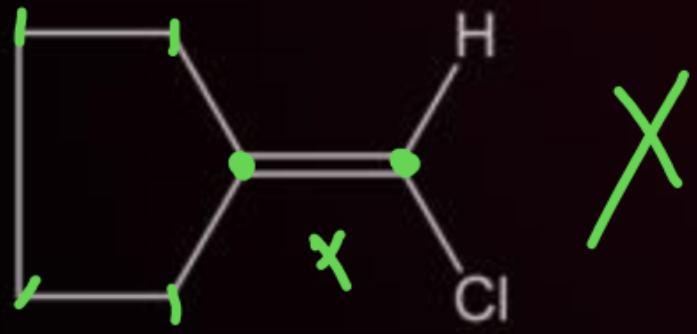


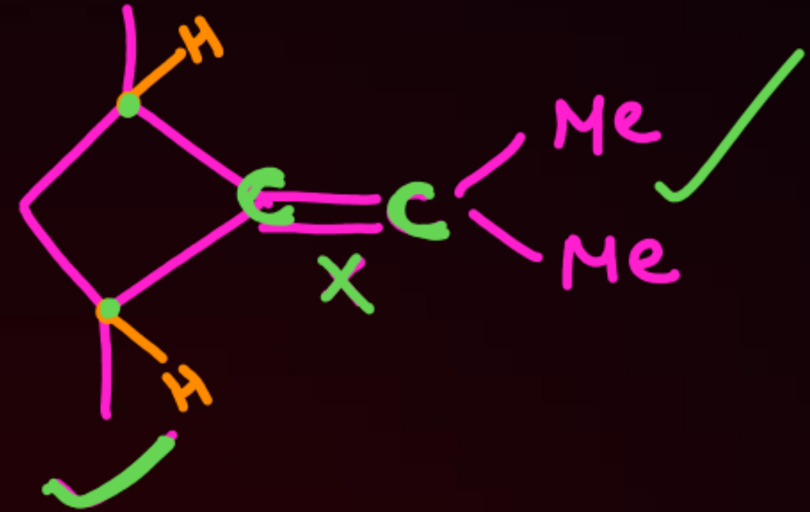
1,1-diphenyl-1-butene

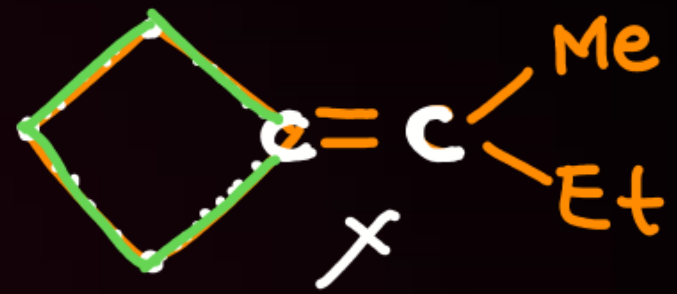


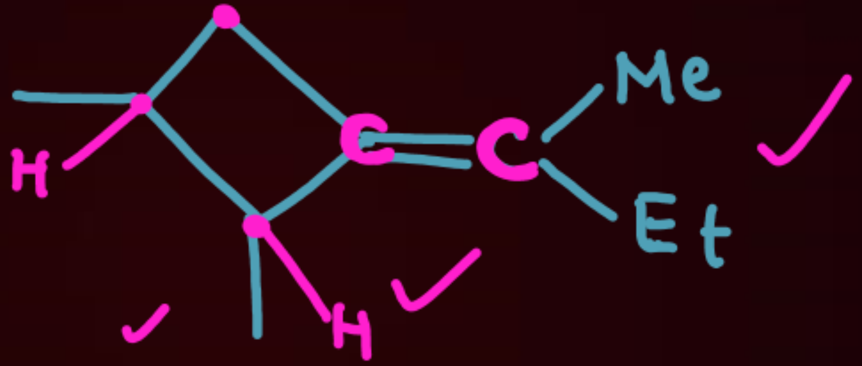

Me
Me
H

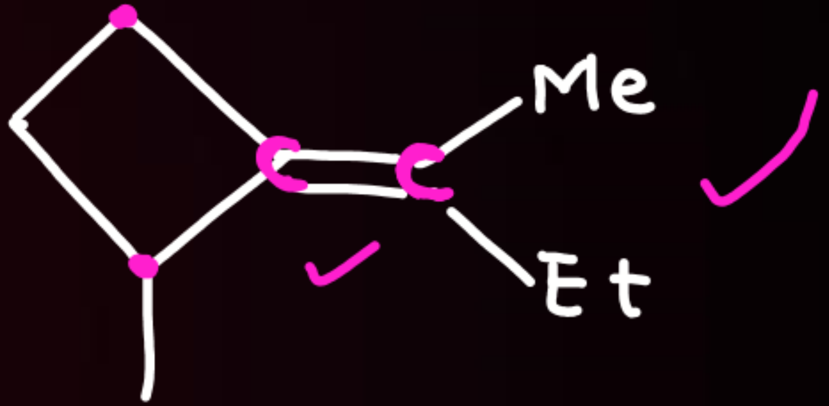

Me
Et
Br


H
Cl

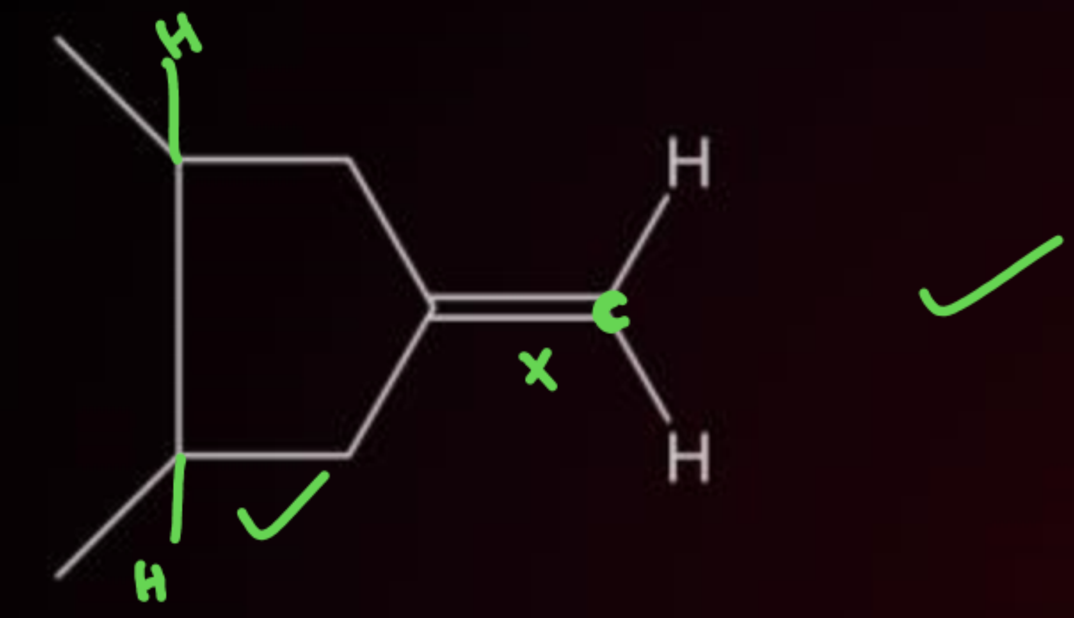

H
Me
Me
H

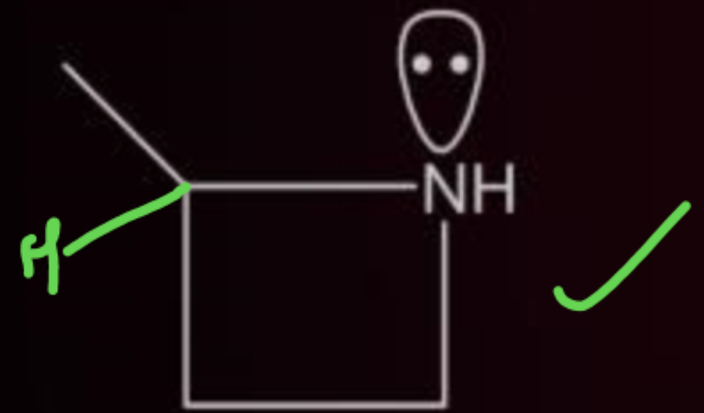

Me
Et

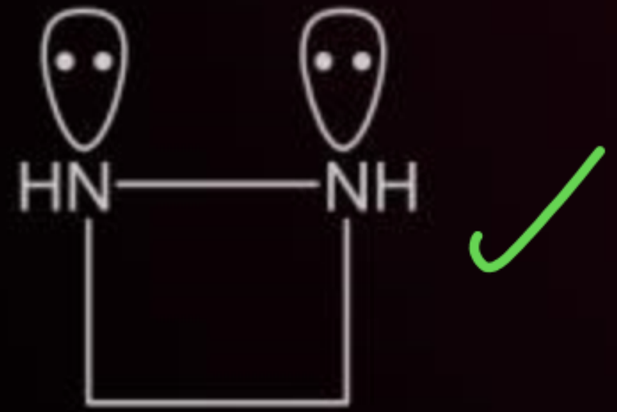

Me
H
Et
H

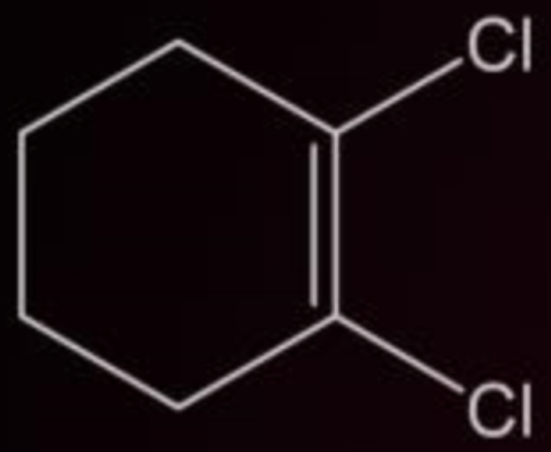

Me
Et


Me
Et

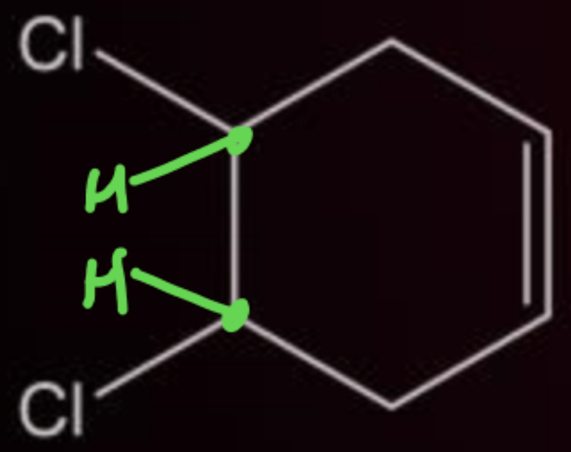

H
H
H
H


NH
H


HN
NH



donot show GI



→donot show GI

GI ✓



cys cyclooctene

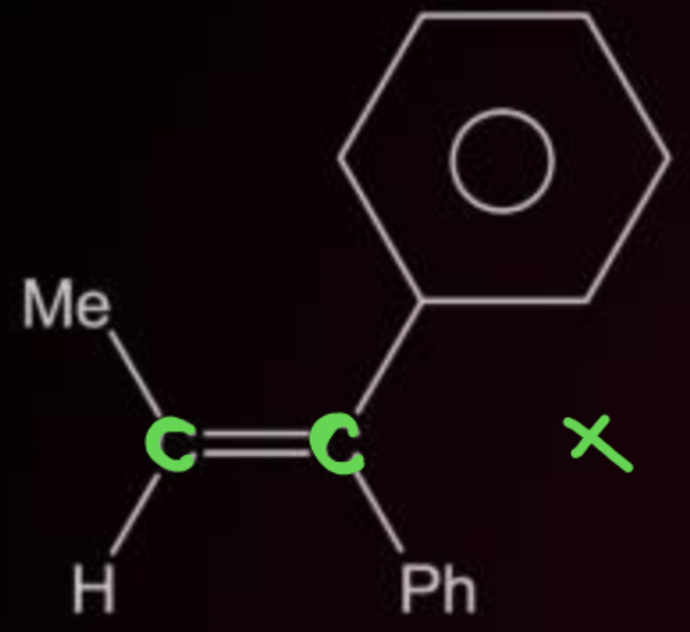


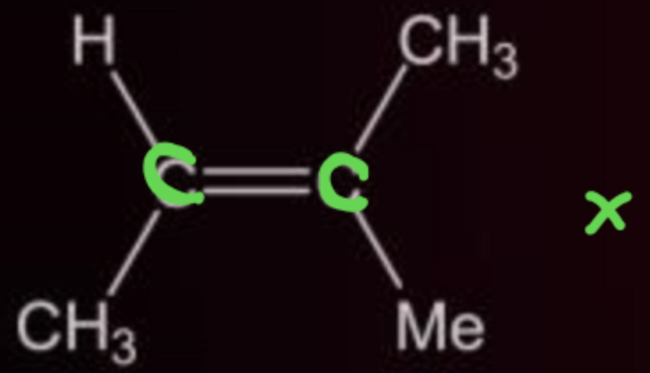
trans cyclooctene

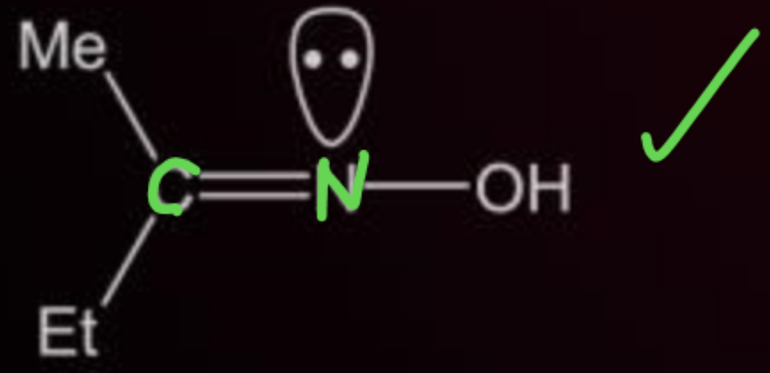
or



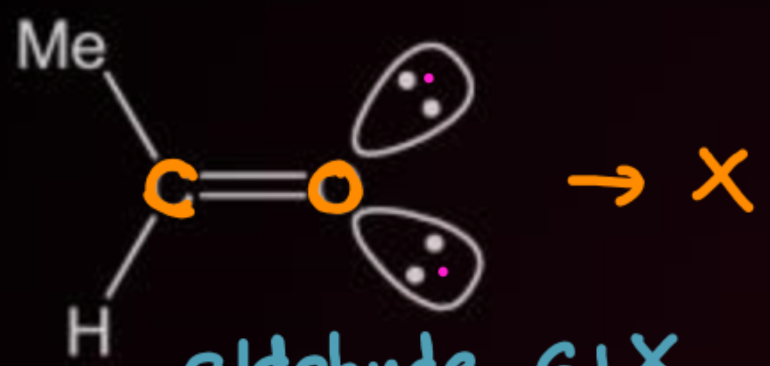
trans cyclooctene


Me
C
C
H
Ph

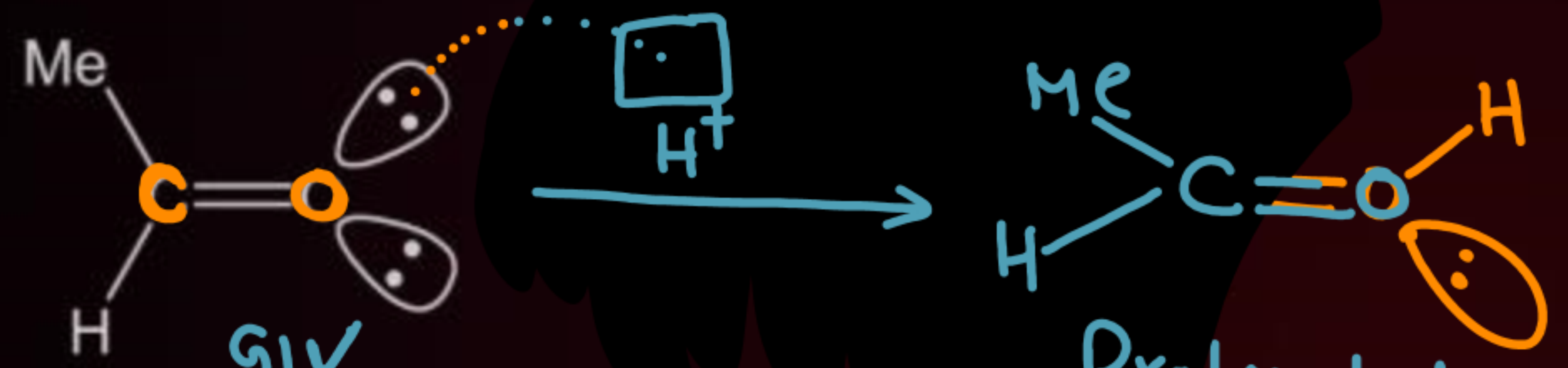

H
CH3
C
C
CH3
Me


Me
C
N
OH
Et

note → aldehyde do not show GI
But
protonated aldehyde shows GI
except protonated Formaldehyde.



aldehyde GI X

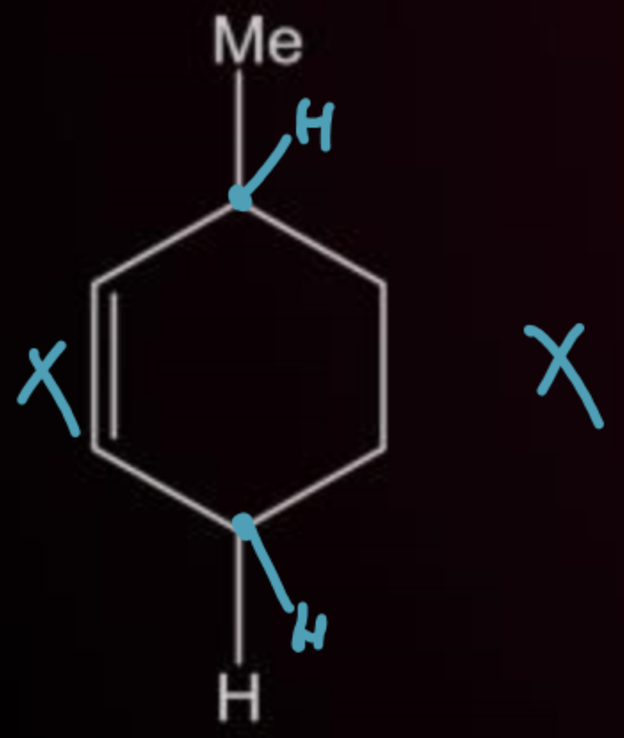


GI X

Protonated aldehyde

GI ✓

GI ✓



Que

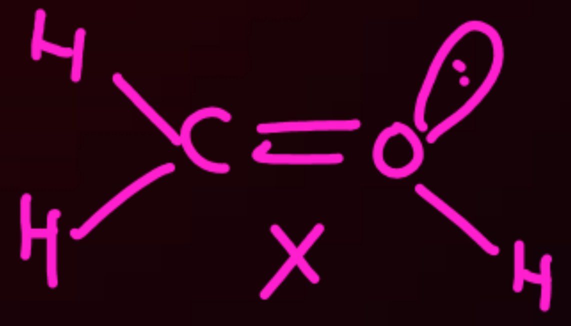
Assertion → All Protonated aldehyde shows GI.

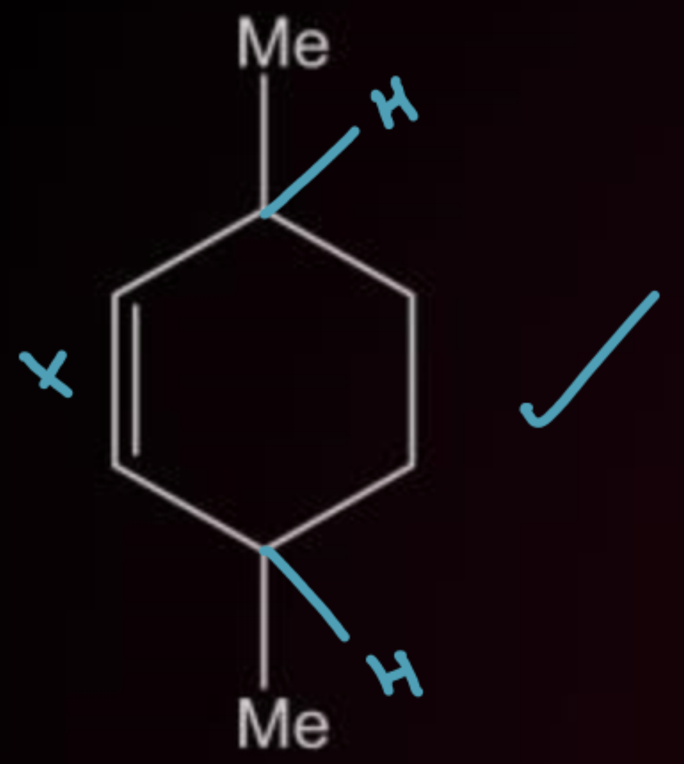
Reason → Pronated Formaldehyde donot Show GI.

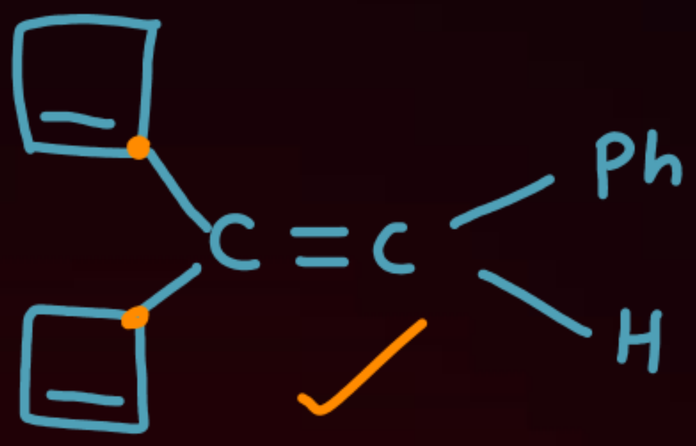
↓

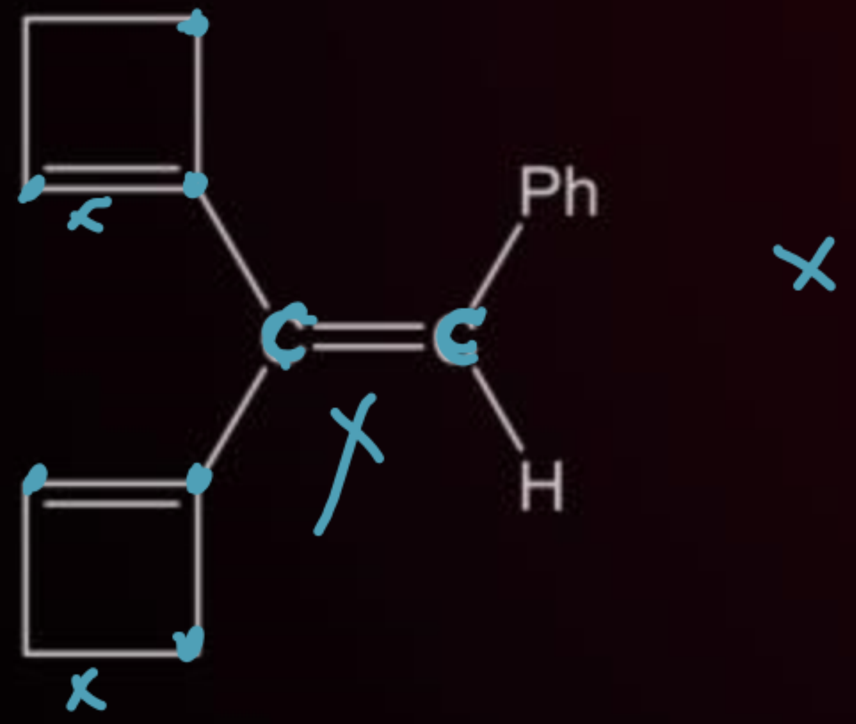
A → false

R → True




Me
H
H
Me

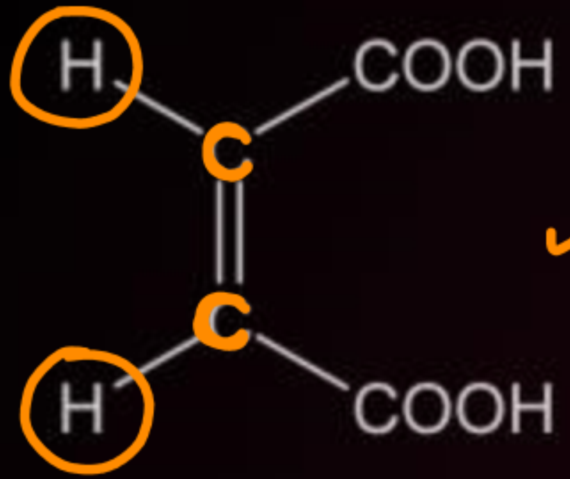

C
C
Ph
H


C
C
Ph
H

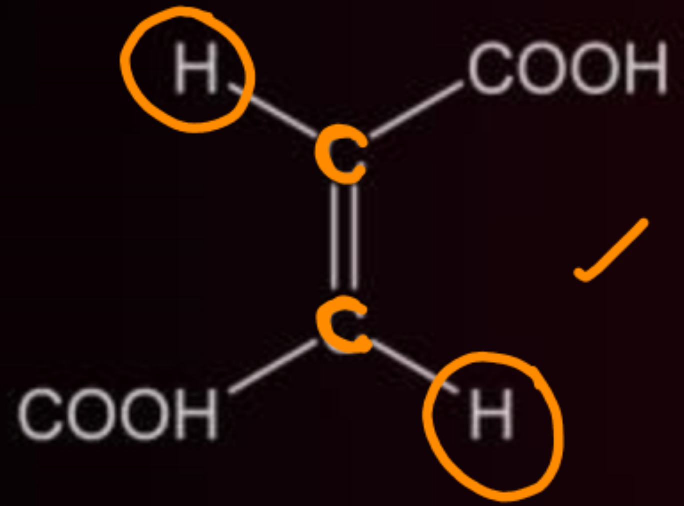
Configuration of GI

cys-Trans

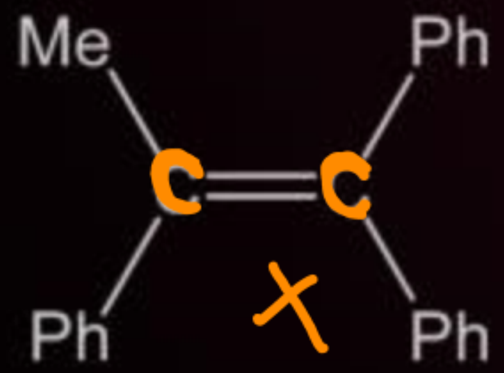
- cys → Same atom or group on same side of RR (same grp = 90°)
- trans → Same atom or group on opposite side of RR (same grp = 180°)



✓ cys (Maleic acid)

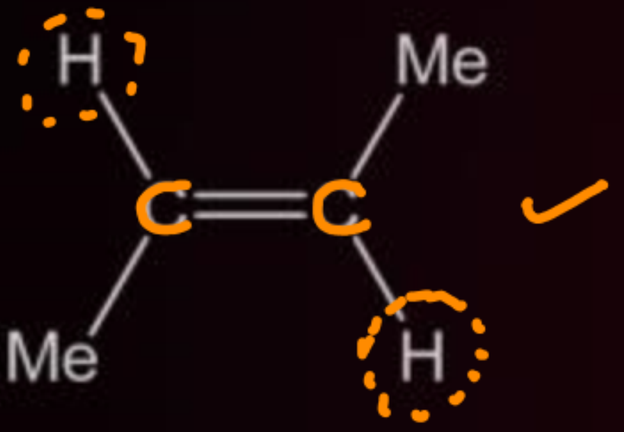


✓ Trans (Fumeric Acid)

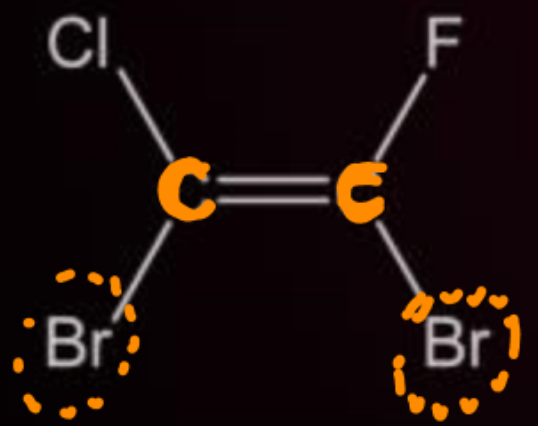




Trans



Trans

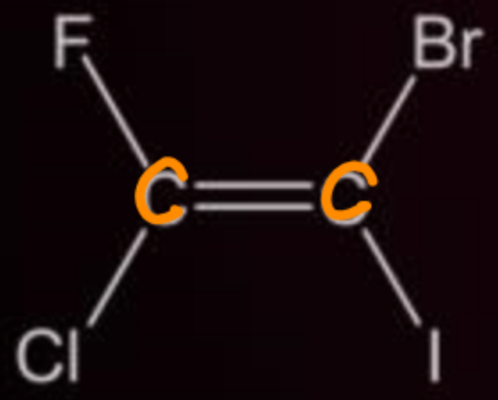


Gl ✓

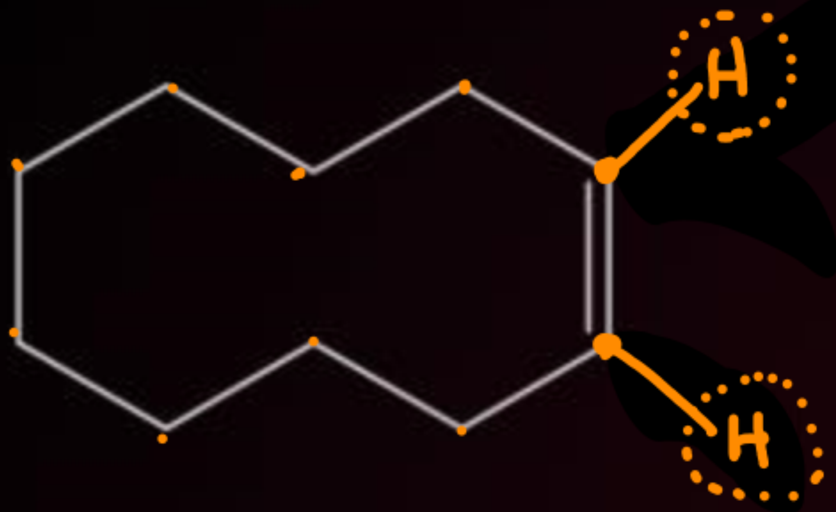
cys



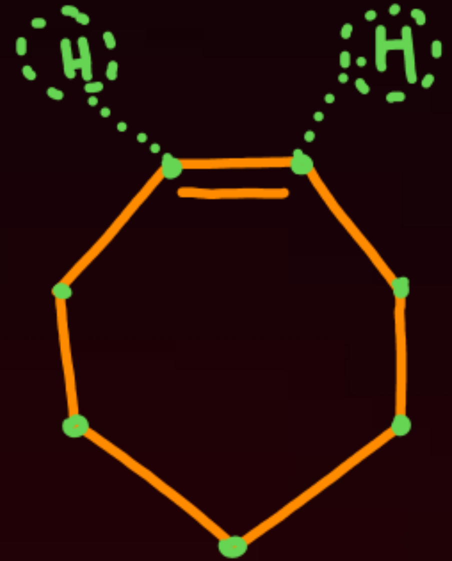
Trans



✓ cys/Trans not define



cys

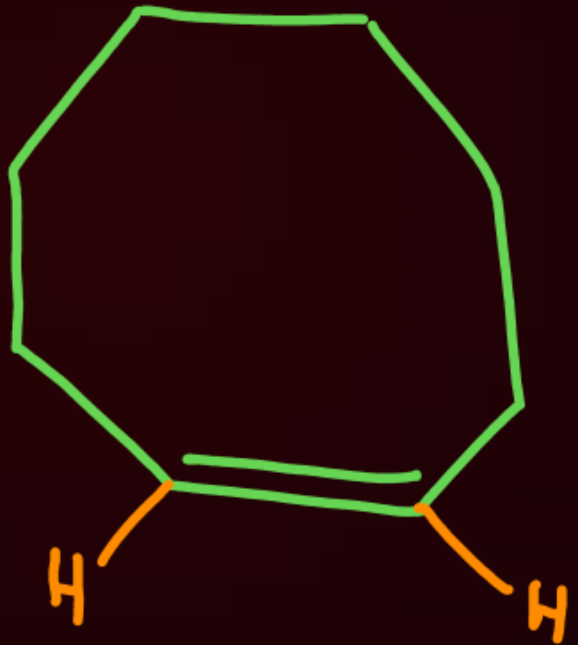


GIX

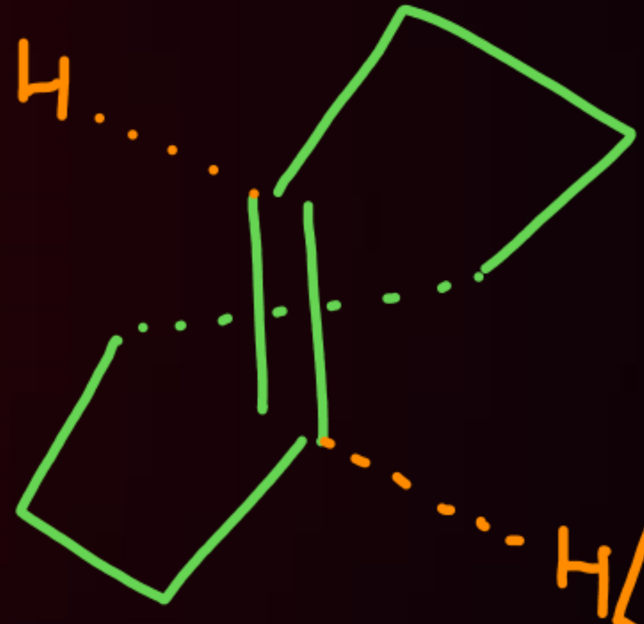


Trans

[redacted]



Cys cyclooctene



Trans Cyclooctene



Trans cyclooctene

E-Z System

Cys → Same group on same side of RR.

Trans → Same group on opposite side of RR.

E → Entigigen → opp side → If Higher Priority group opp side ⇒ E

Z → Zusammen → same Side → If Higher priority group on Same Side ⇒ Z

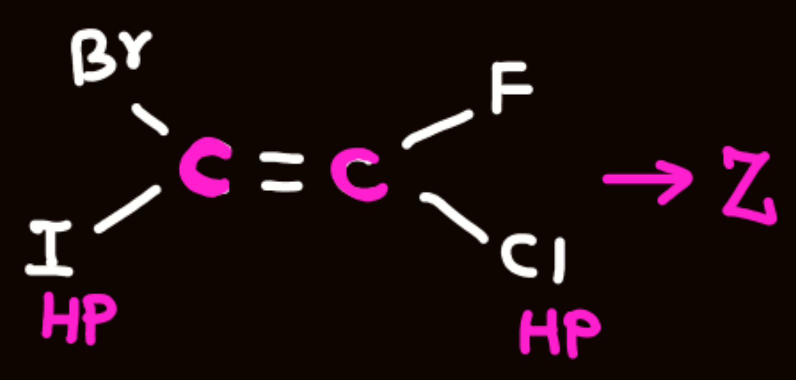
⇓

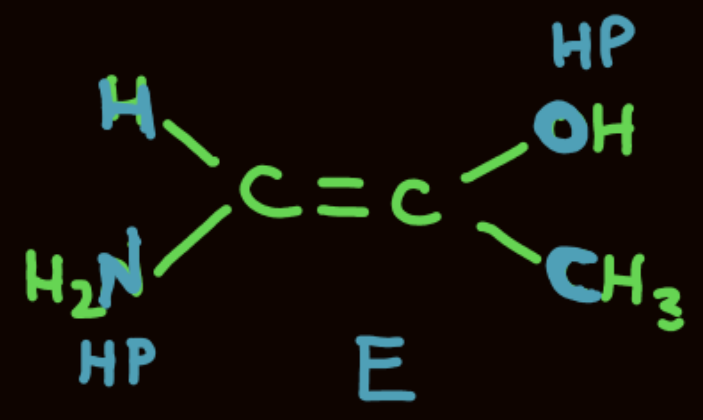
German word

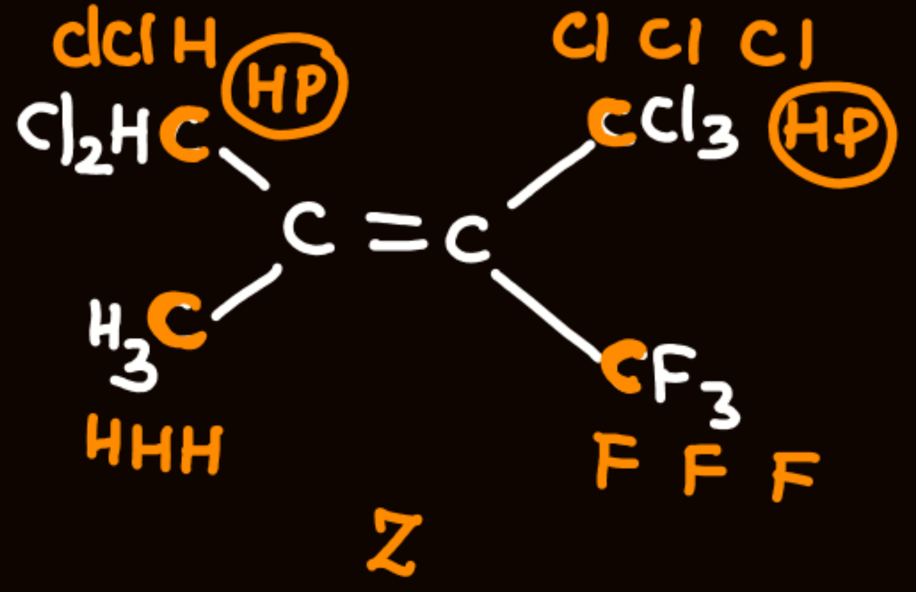
CIP Rule / Priority Rule

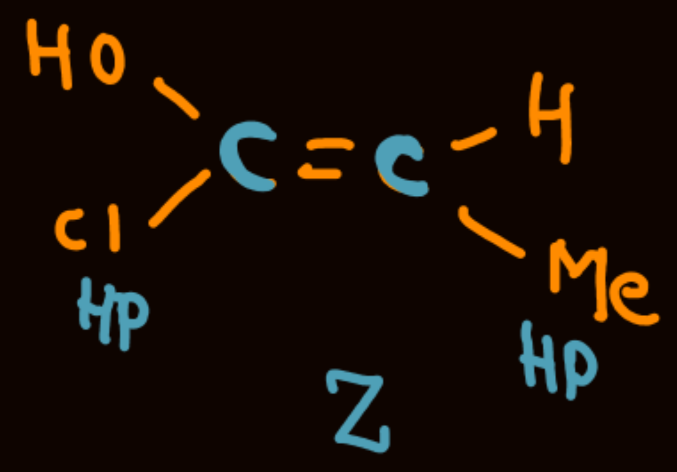
Cahn Ingold Prelog Rule

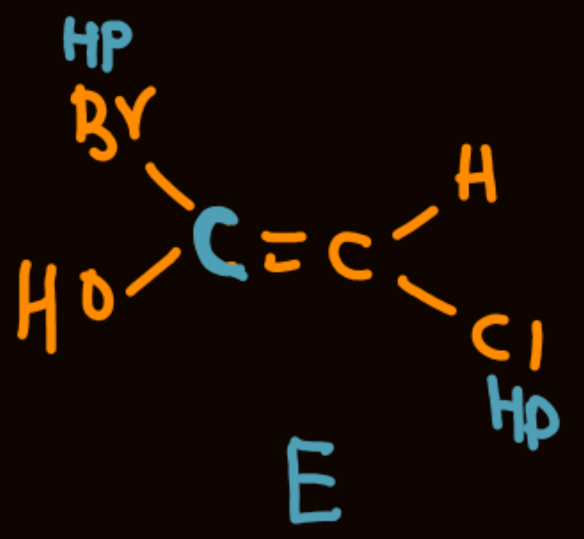
Rule 1 → Priority ∝ atomic num of atom directly attached to sp^2 carbon.

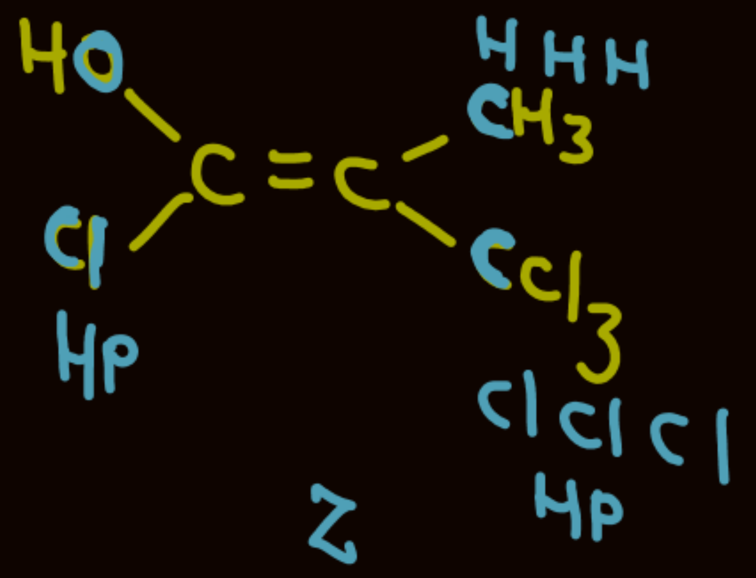












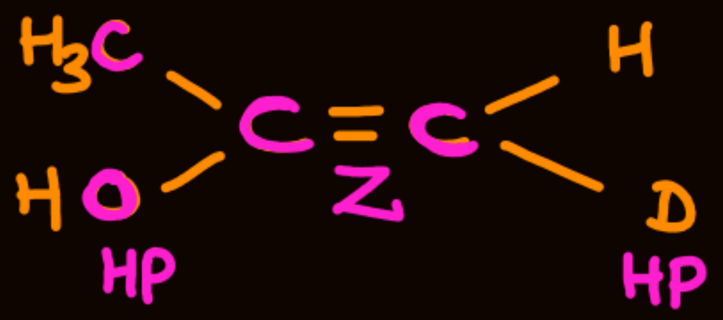
If atomic no is same → Isotope

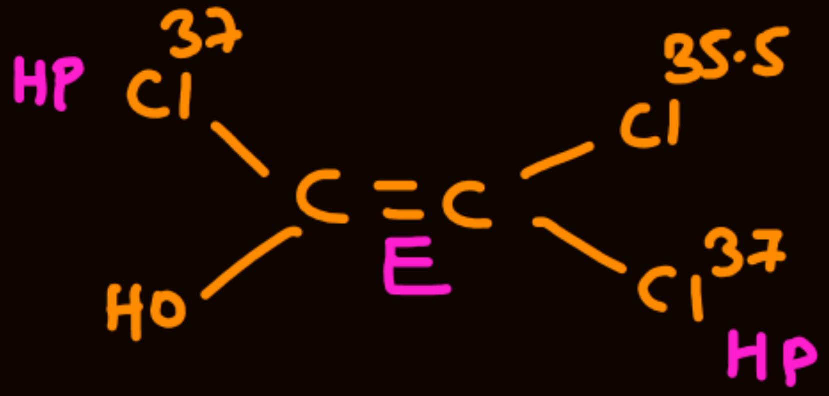
Rule2 → Priority ∝ atomic mass of isotope

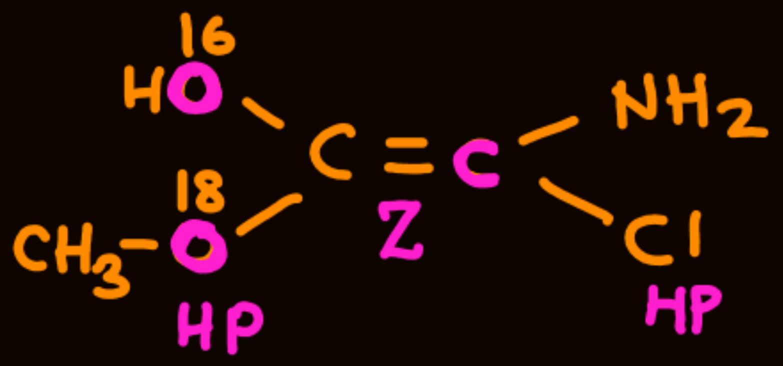
$^{1}_{1}H < ^{2}_{1}D < ^{3}_{1}T$

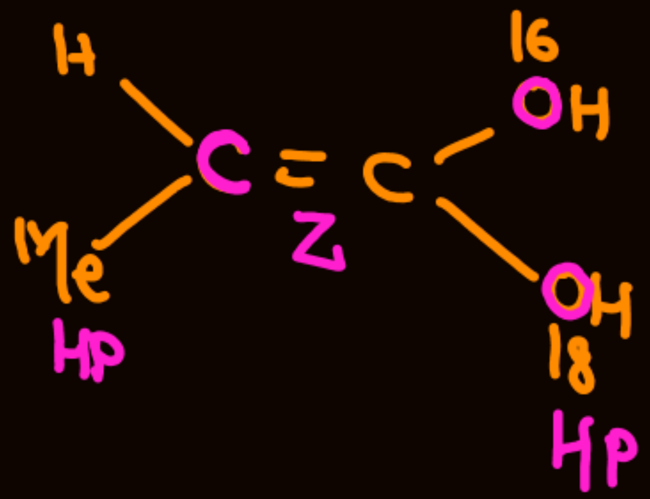
$Cl^{35.5} < Cl^{37}$

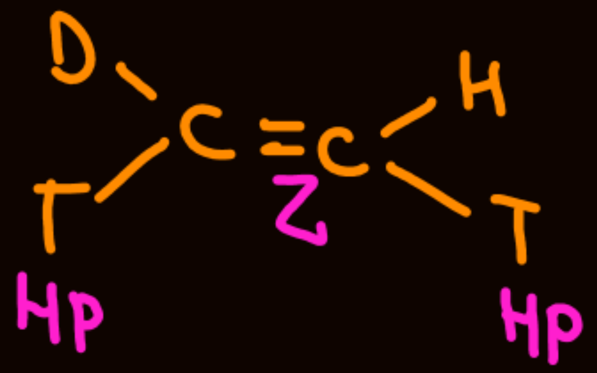
$O^{16} < O^{18}$

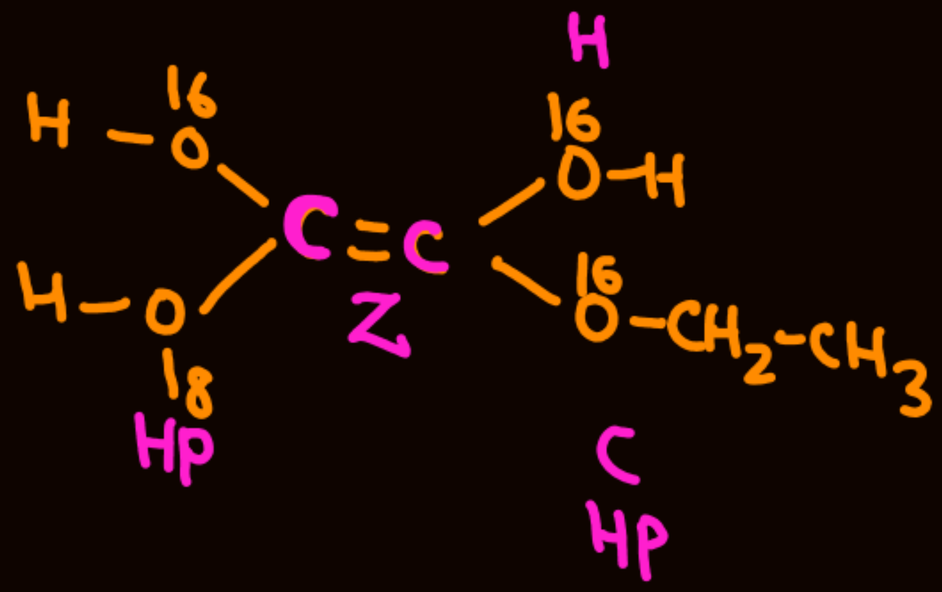












Challange

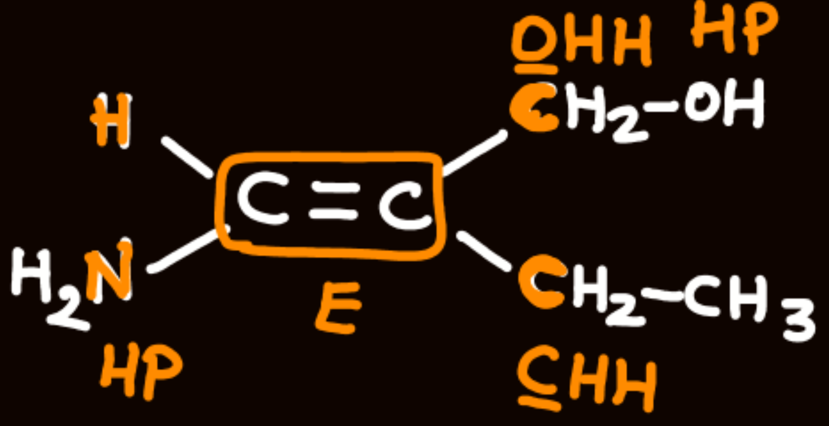
5 timer

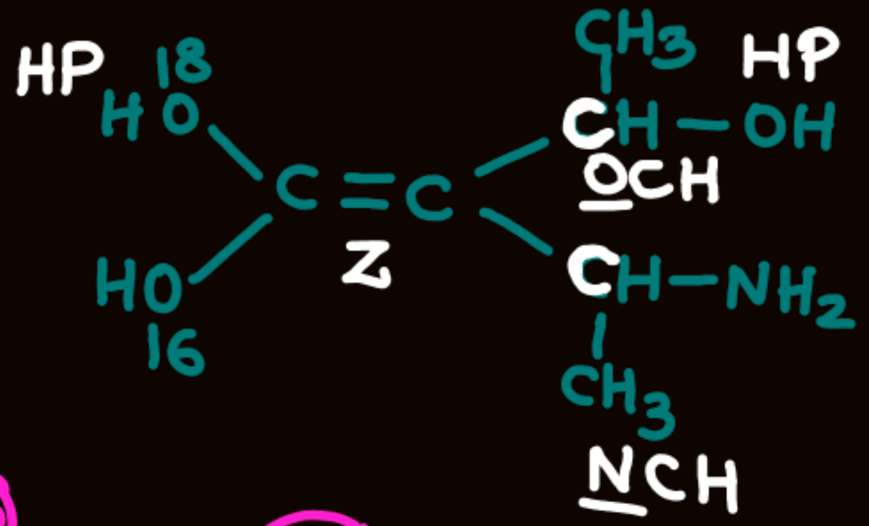
25	25	25	25	25

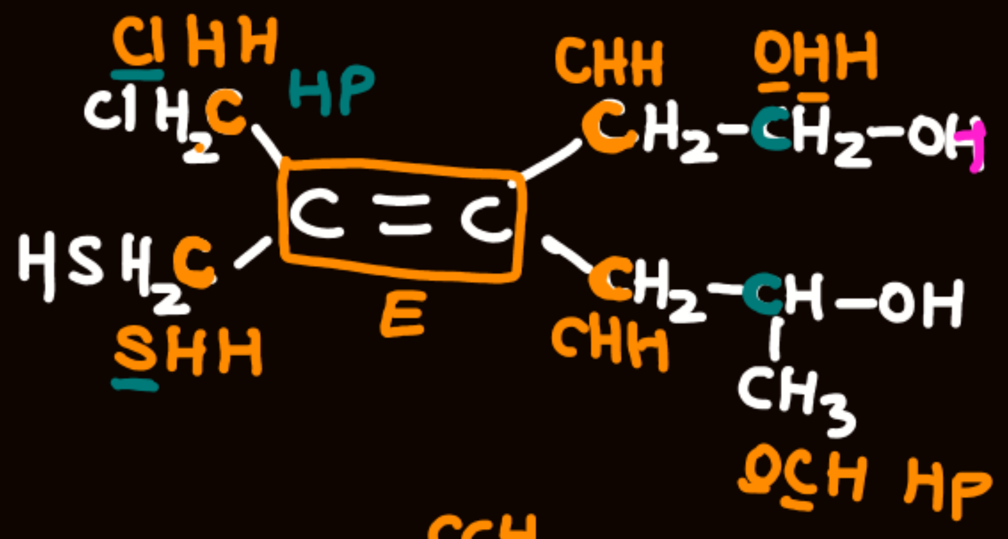
THANK YOU
All the Best!!

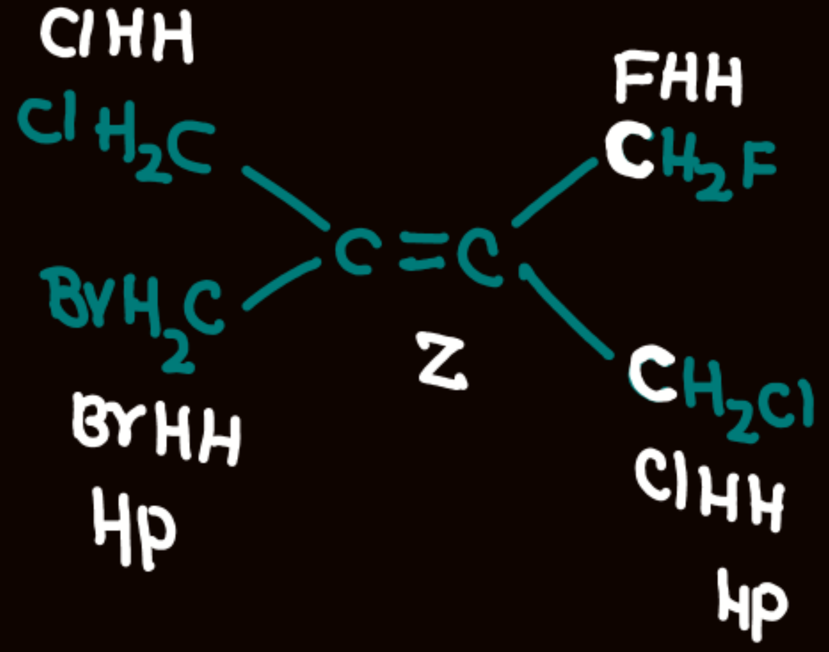
CIP Rule

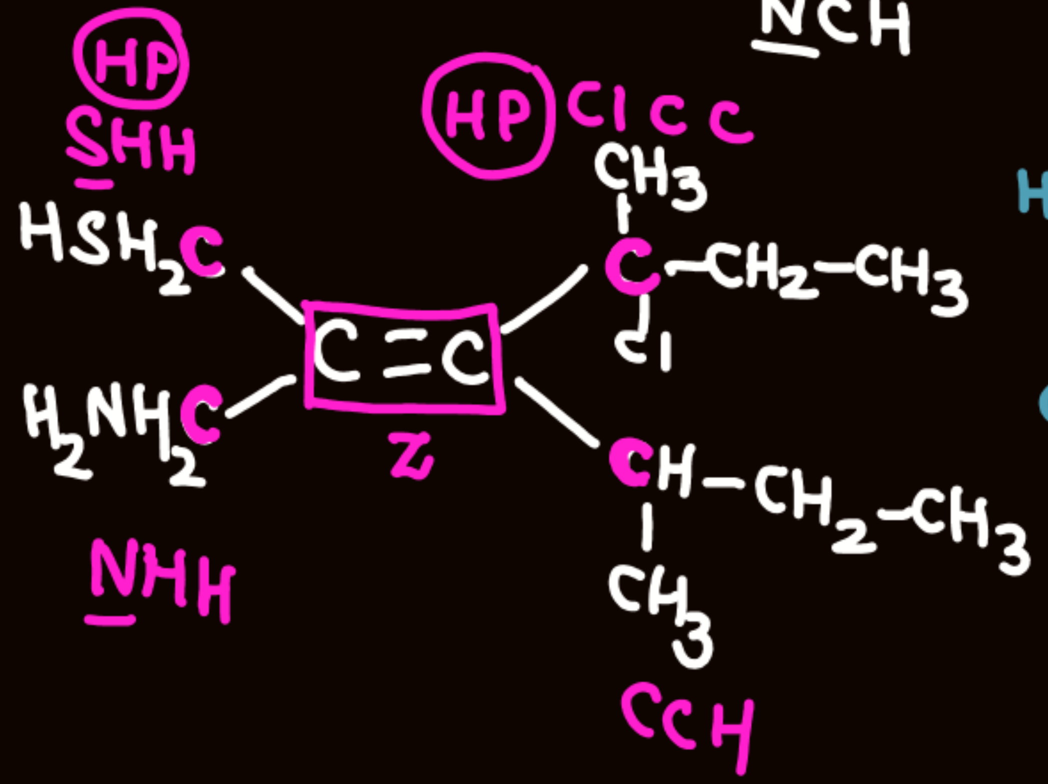
Rule 3 → If directly attatched atom is Same then write the bonds in decreasing order of atomic number.

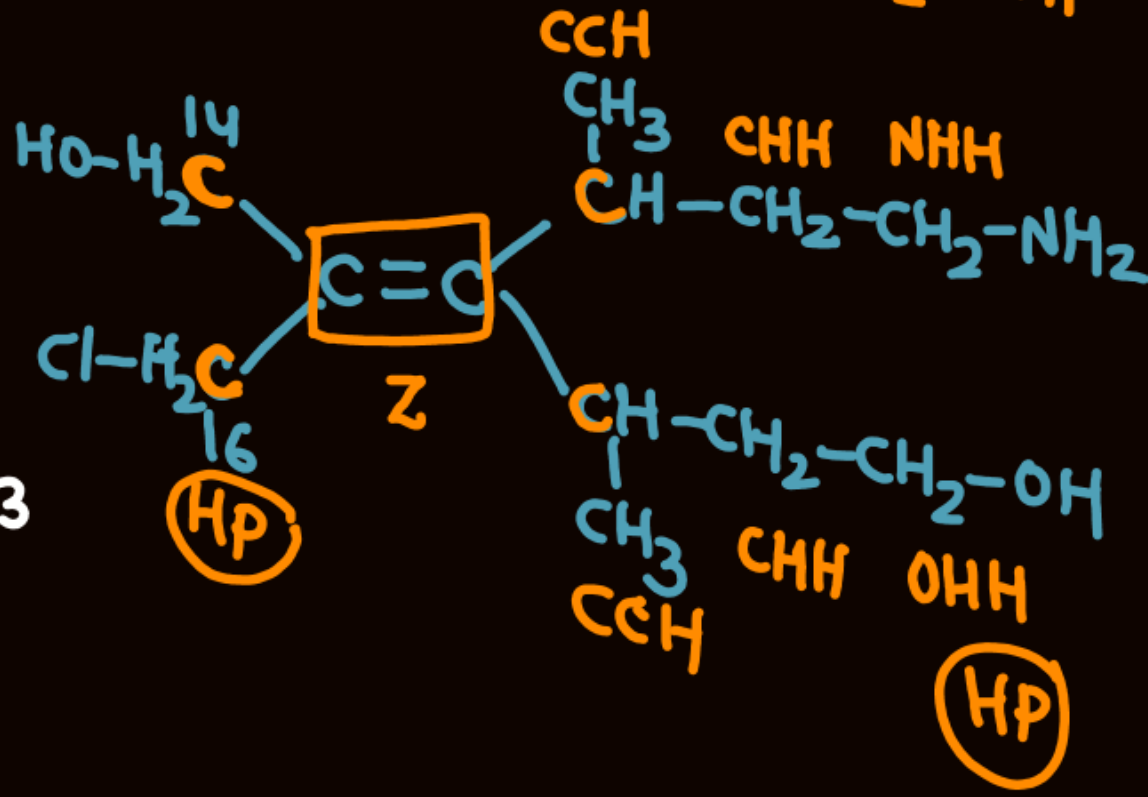


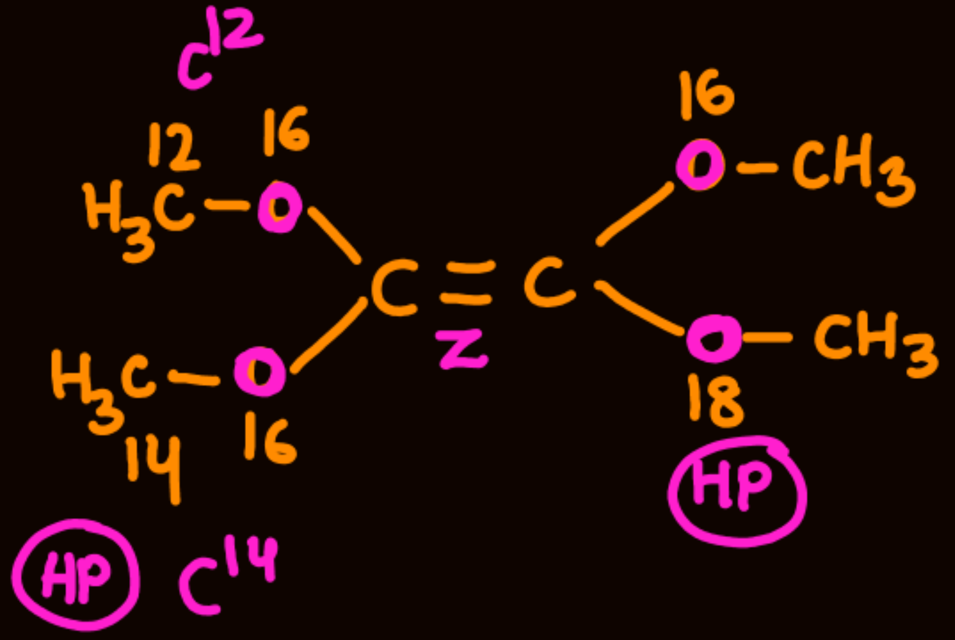


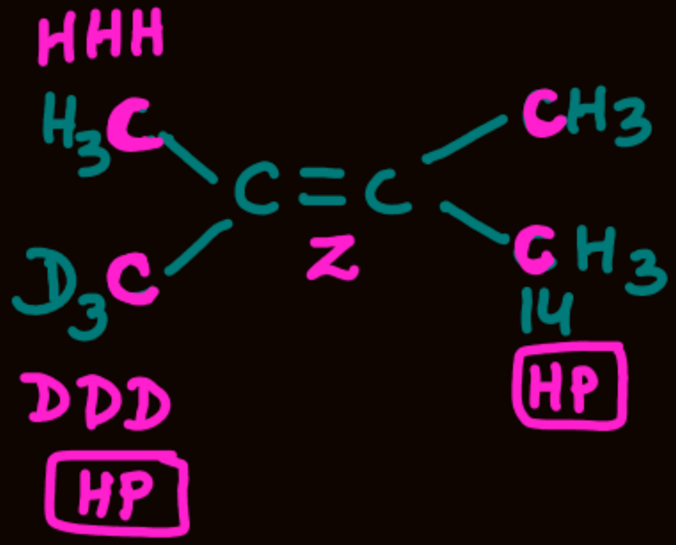


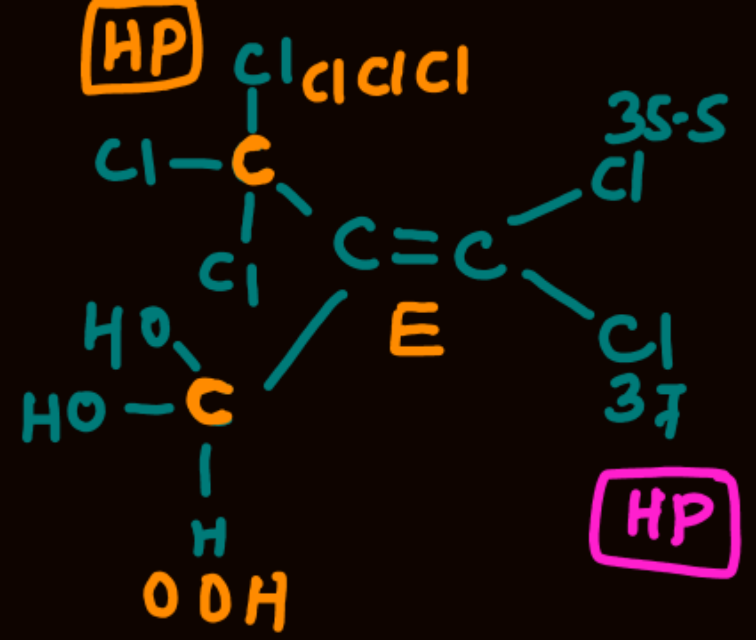




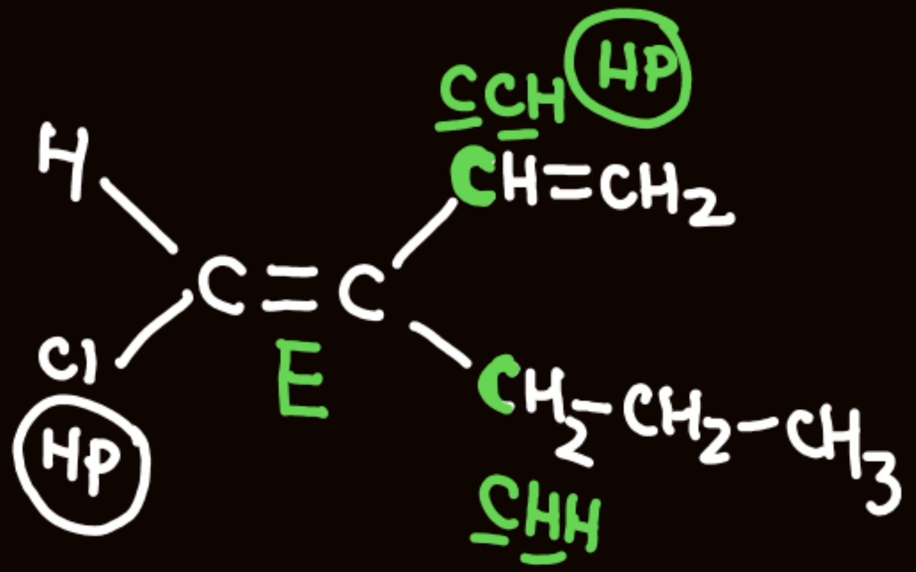


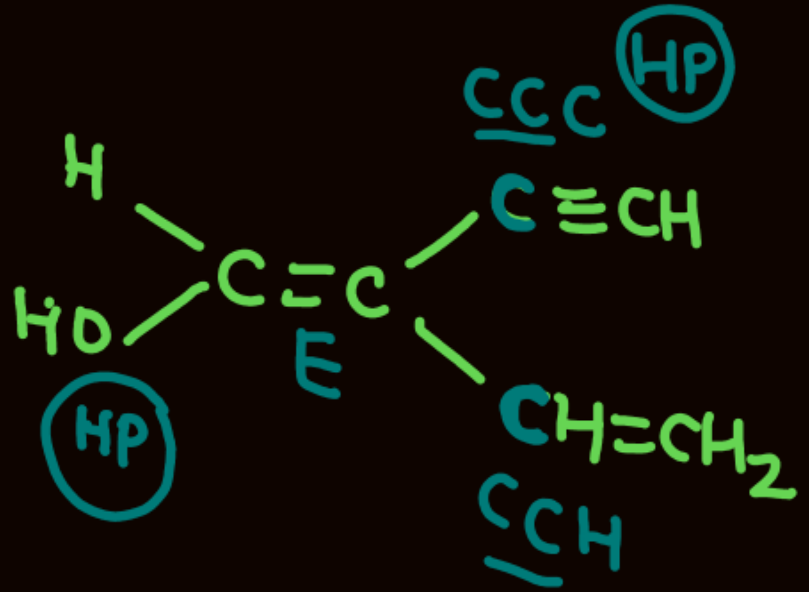


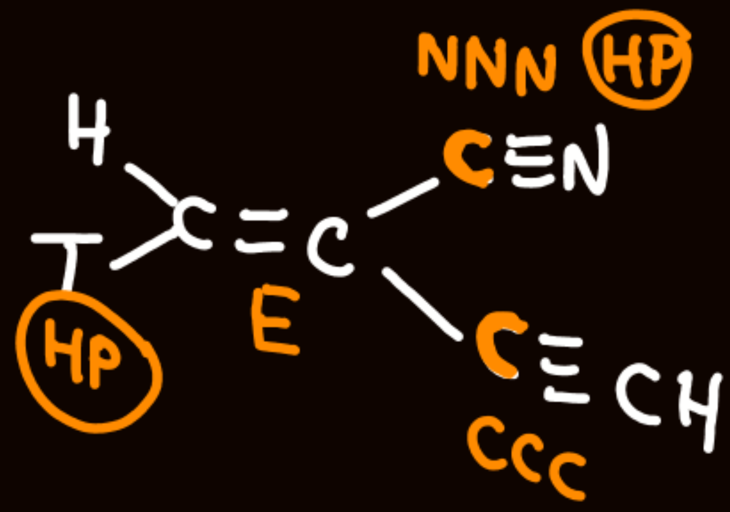


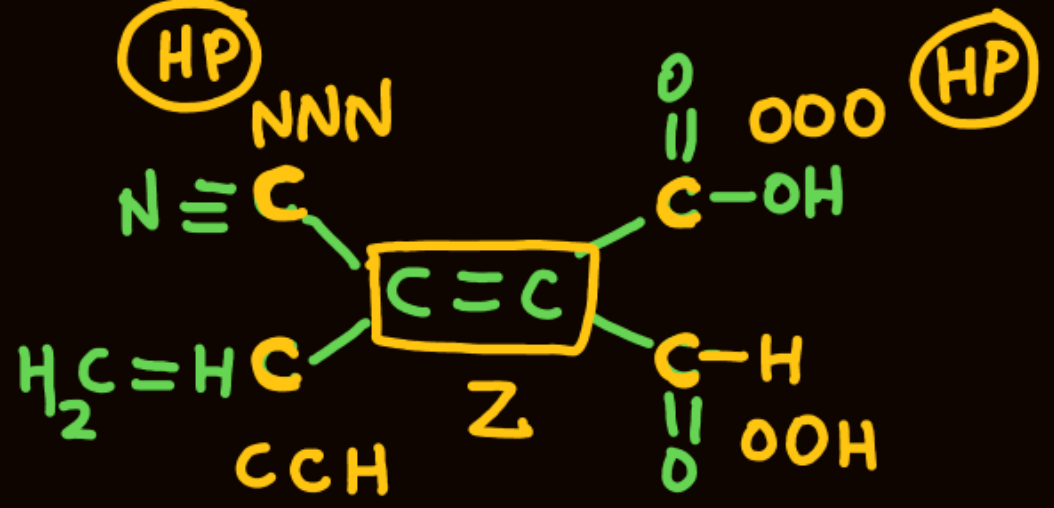


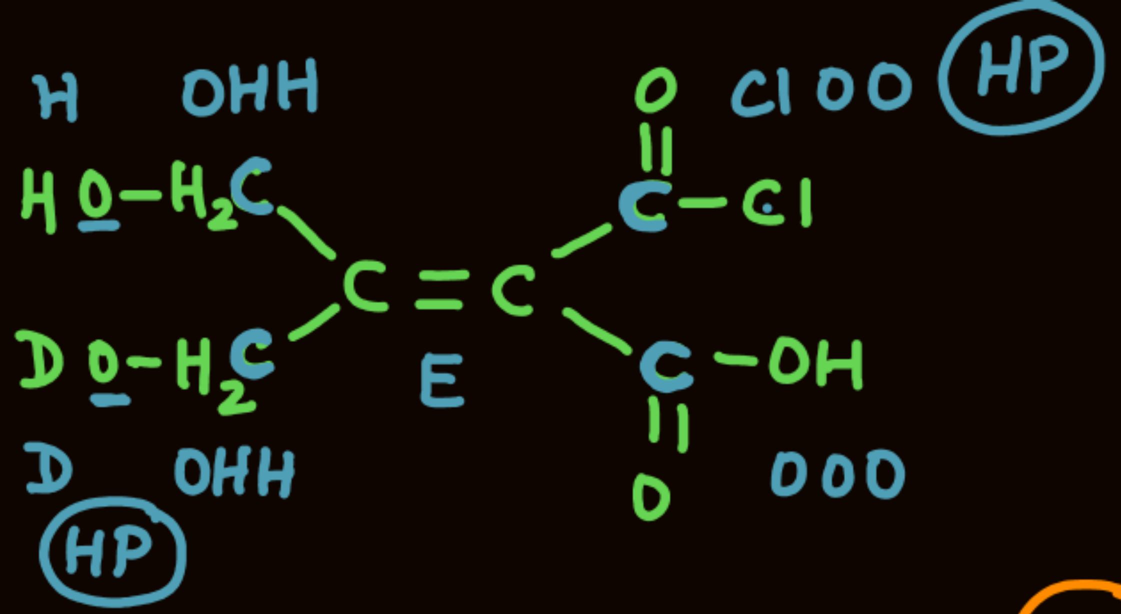
Rule 4 → If directly attached atom has multiple bond then write dummy atom (Imaginary) for multiple bond & decide priority.

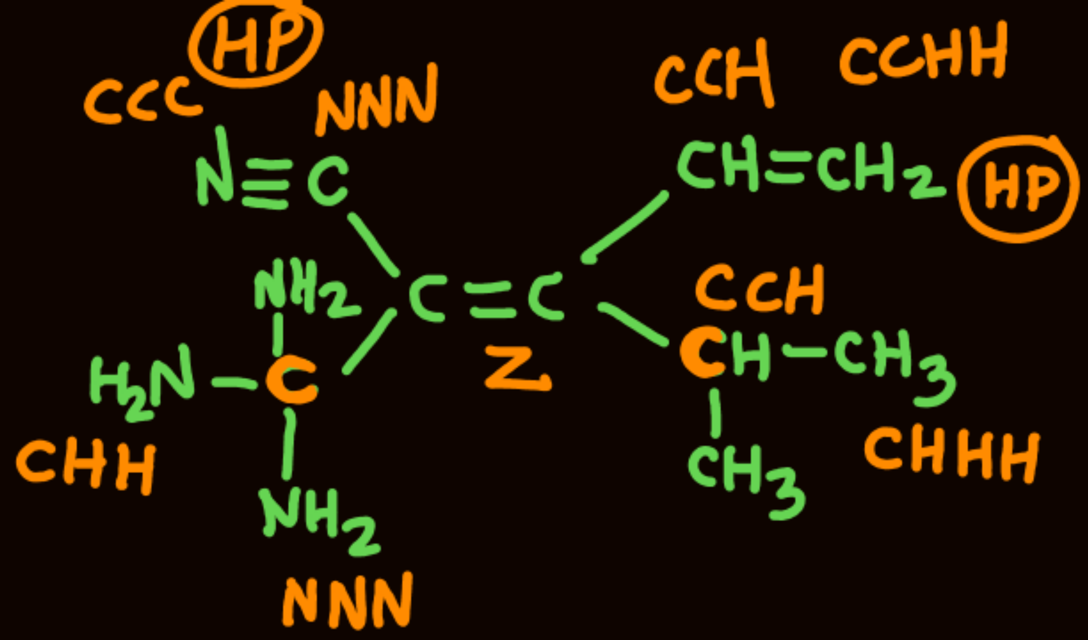


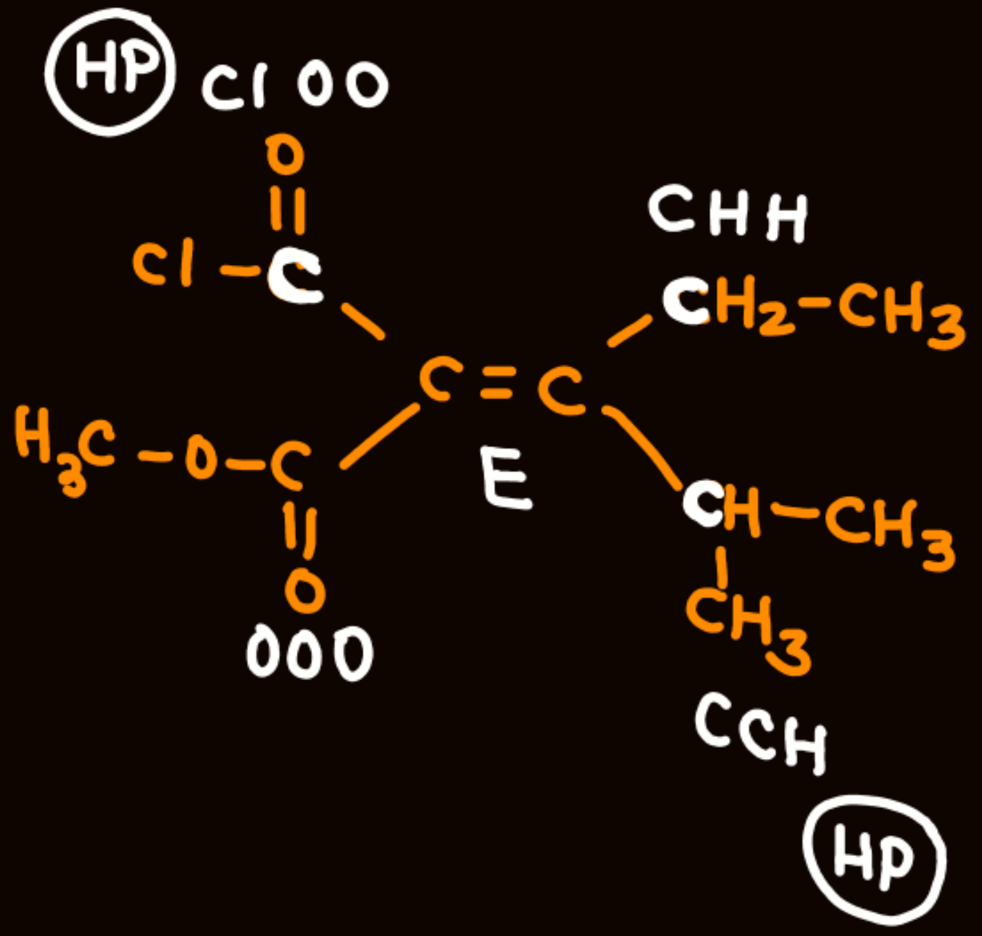


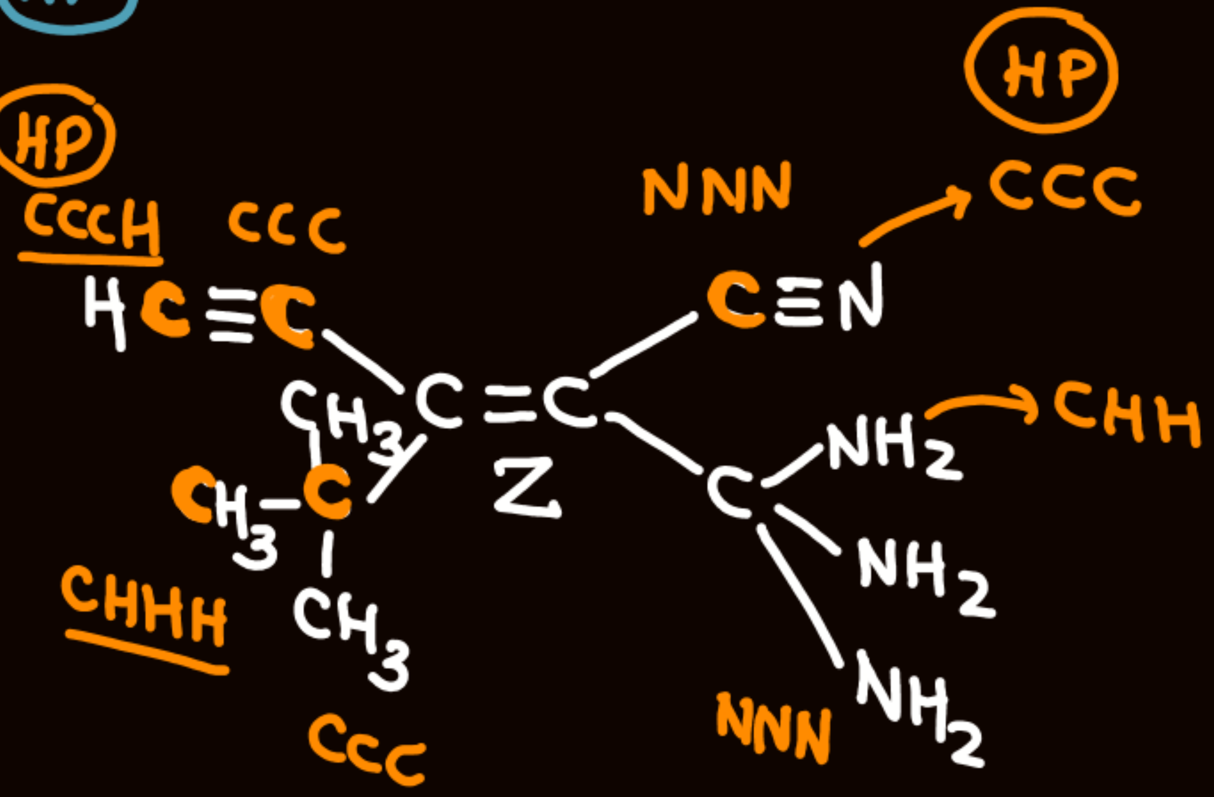


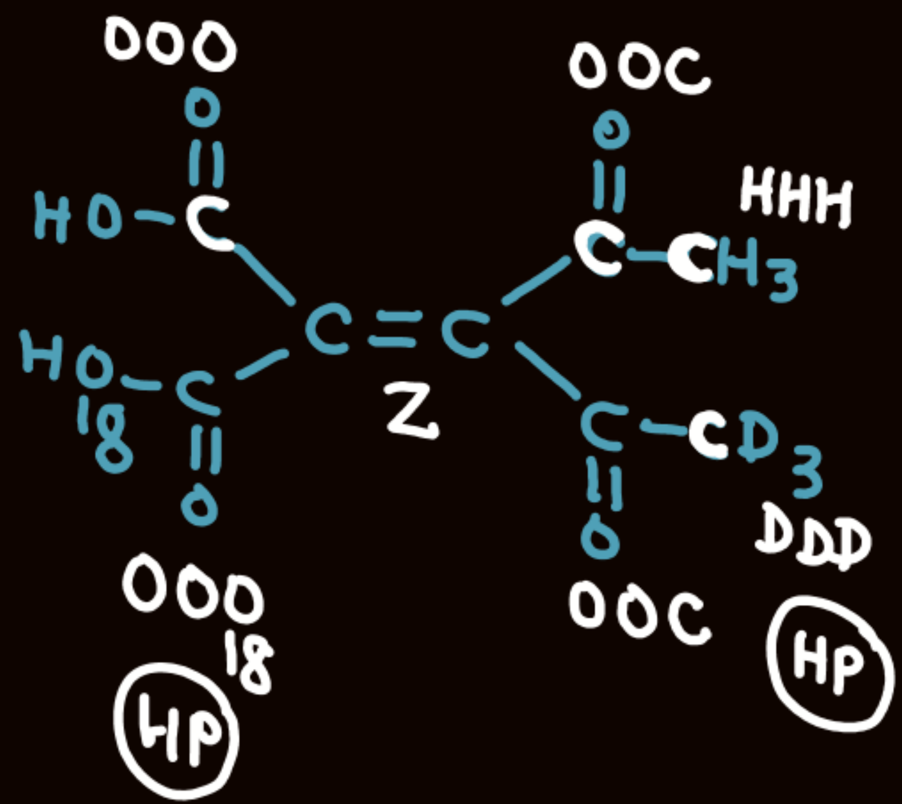




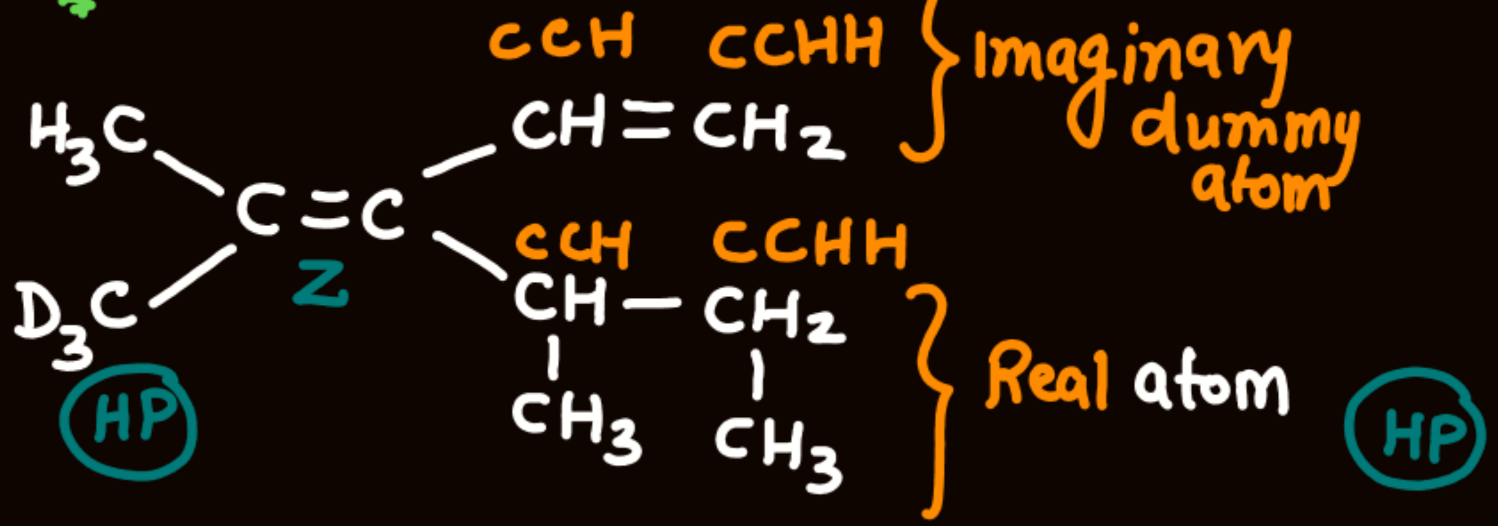




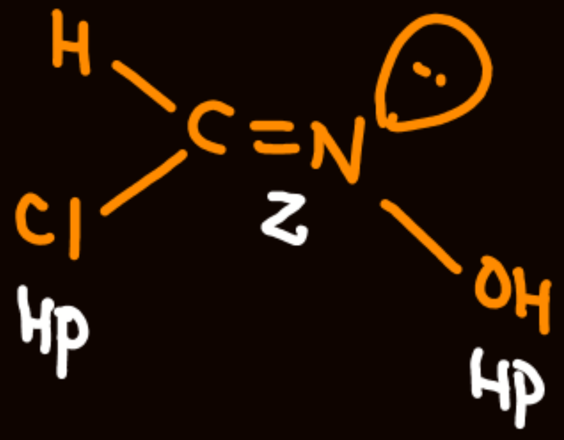




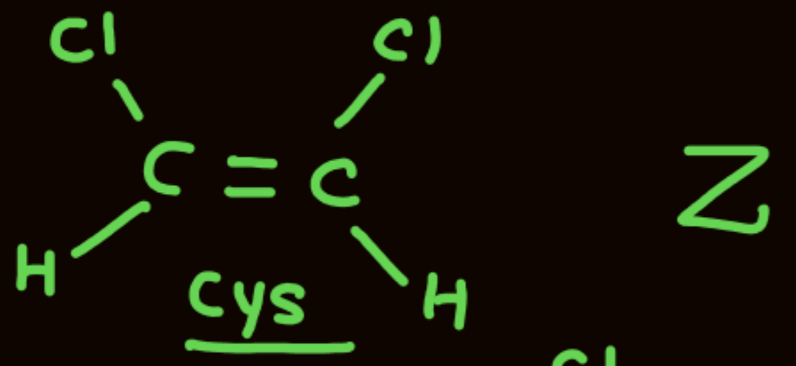
note : B/w Real & Imaginary → Real has the higher priority.

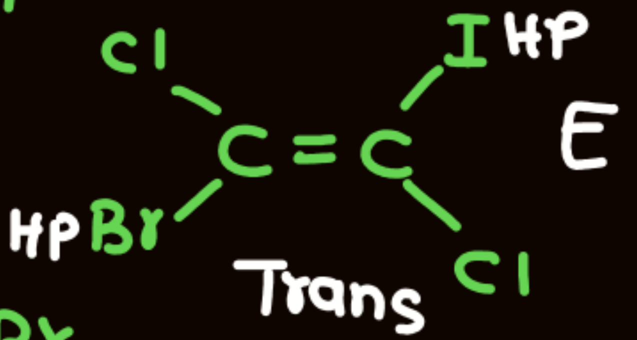


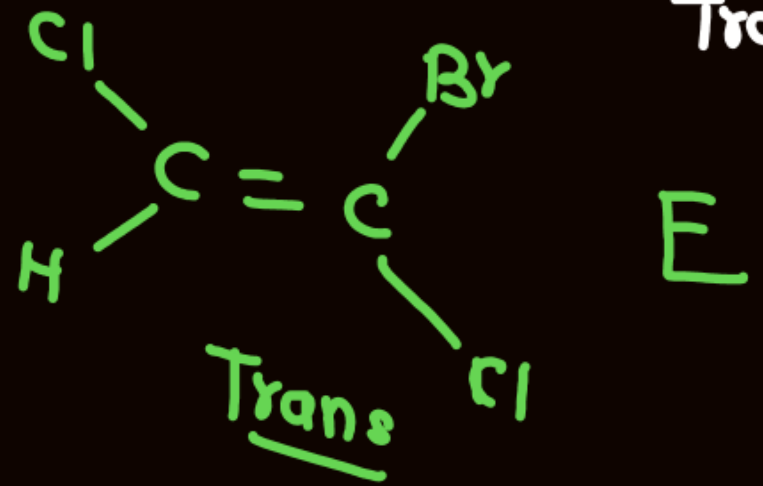
note : Lonepair always gets Lower priority.



note → E, Z has no relation with cys-Trans.

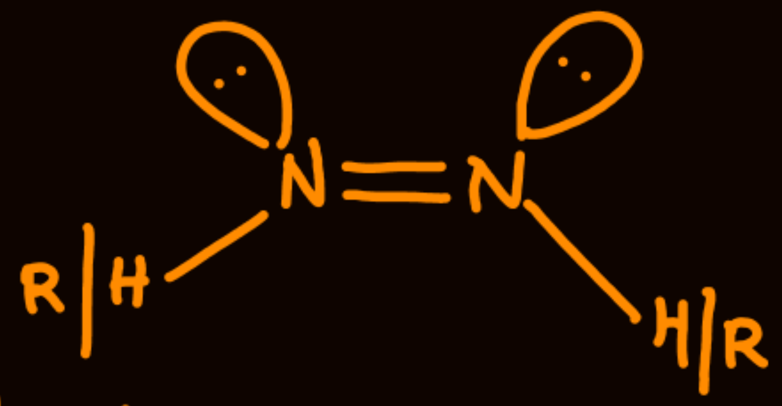






Syn-Anti Configuration

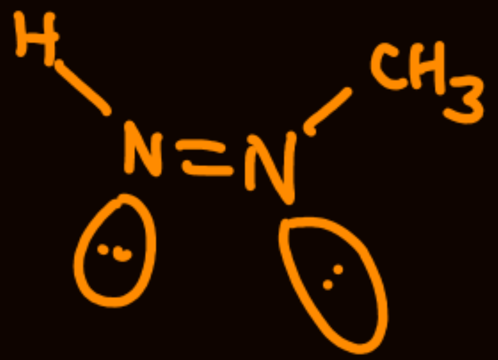
azo comp



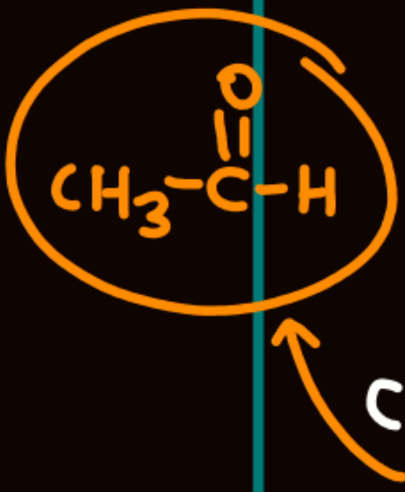
* lonepair – Same side ⇒ Z
* lonepair – opp Side ⇒ E



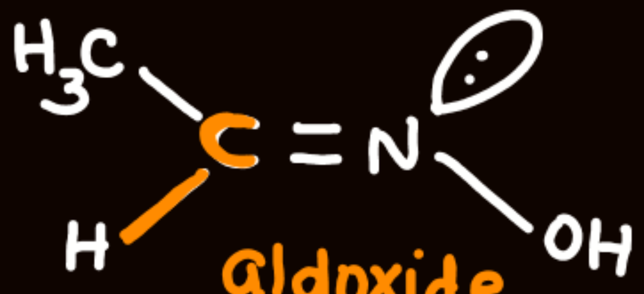
E



Z



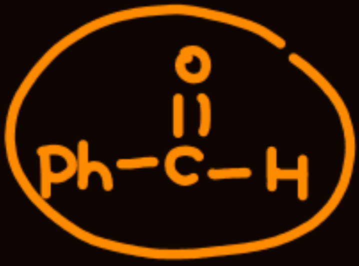
oxime comp

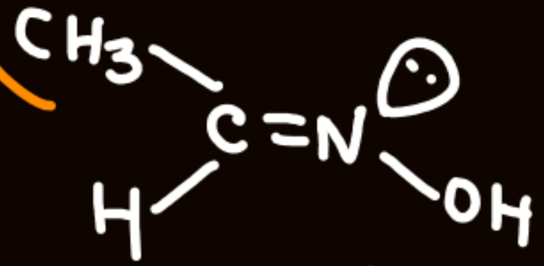


aldoxide

H & OH → Same Side → Syn

H & OH → opp Side → Anti

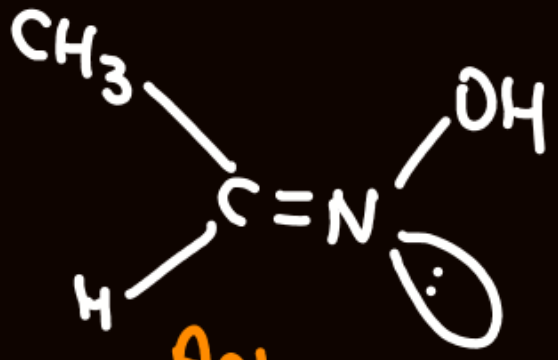




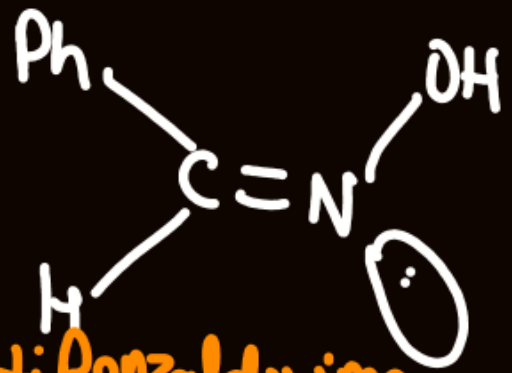
Syn acetaldoxime



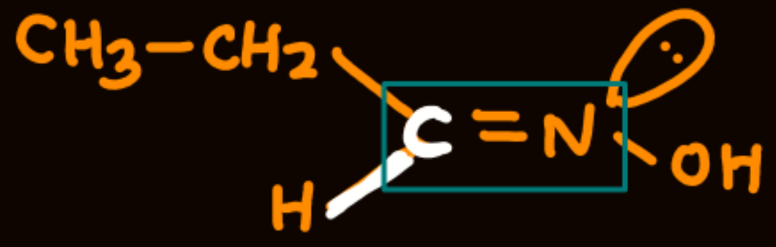
Syn Benzaldoxime



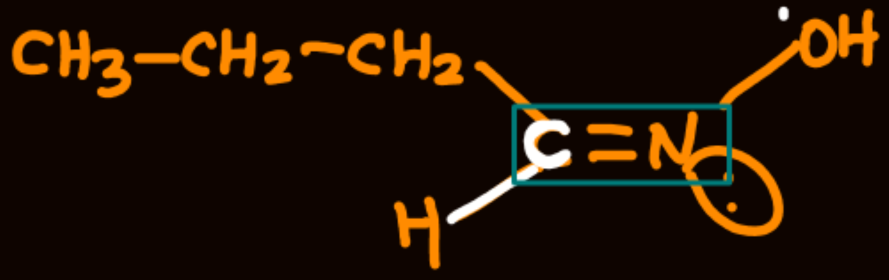
Anti acetaldoxime



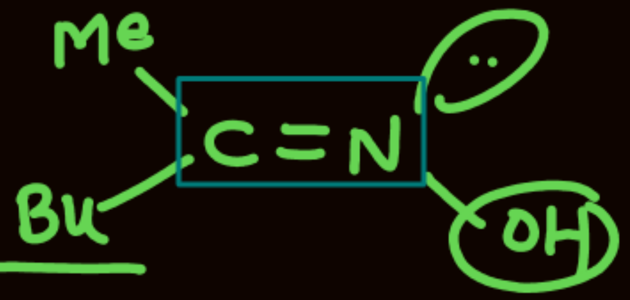
Anti Benzaldoxime



Synpropionaldoxime

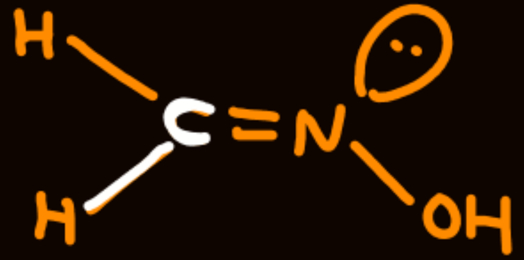


Anti butyraldoxime



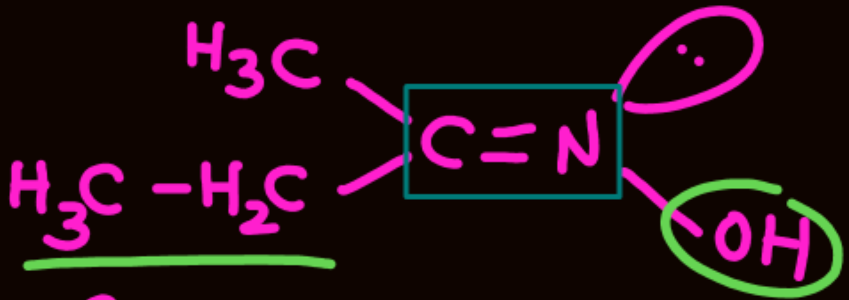
Syn Butylmethyl ketoxime

Anti methyl Butyl ketoxime



Syn ✗

donot show GI



Syn ethylmethyl ketoxime

Anti methyl ethyl ketoxime

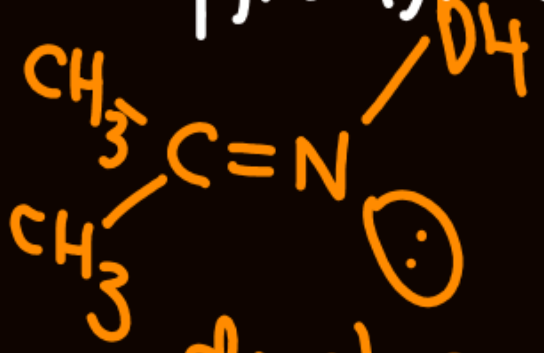


Syn Butyl Propyl ketoxime

Anti Propyl Butyl Ketoxime

note → all oxime (^aldo) show GI except oxime of formaldehyde.

→ all ketoxime show GI except oxime of Symmetrical ketone.



donot show GI.

Counting of Total Geometrical Isomers

Unsymmetrical

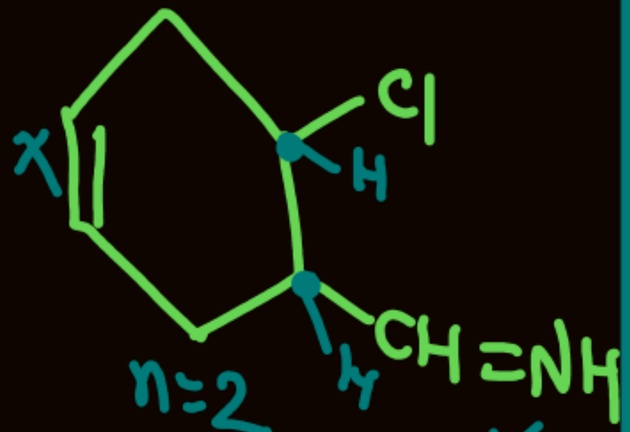
* $TGI = 2^n$

n = RR showing GI

$CH_3-CH=CH-CH_2-CH_3$ ✓

$n = 1$

$TGI = 2^n$
$= 2^1$
$= 2$



$n = 2$

$TGI = 2^2$
$= 4$

Symmetrical

* $TGI = 2^{n-1} + 2^{P-1}$

n = RR showing GI

$P = \frac{n}{2}$ n = even

$P = \frac{n+1}{2}$ n = odd

$CH_3-CH=CH-CH_3$ ✓

$n = 1$

$P = \frac{1+1}{2}$

$P = 1$

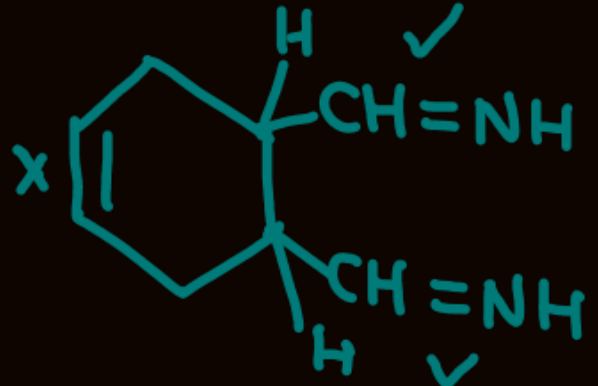
$2^{n-1} + 2^{P-1}$

$2^{1-1} + 2^{1-1}$

$2^0 + 2^0$

$1 + 1$

2



$n = 3$

$P = \frac{3+1}{2} = 2$

$TGI = 2^{n-1} + 2^{P-1}$

$= 2^2 + 2^1 = 6$

THANK YOU
All the Best!!

Total Number of G.I.

Case 1:

When molecule is unsymmetrical.

Total G.I. = 2^n

Where n = number of R.R (Restricted Rotation) showing G.I.

Case 2:

When molecule is symmetrical

Total G.I. = $2^{n-1} + 2^{p-1}$

n = number of RR showing G.I.

n = odd $p = \frac{n+1}{2}$

n = even $p = \frac{n}{2}$

Que Cal Total num of Geometrical isomers in the following Compound.

Q.1. $CH_3 - CH = CH - (CH = CH) - CH_2 - CH_3$

Unsymmetrical

$n = 2$

$TGI = 2^n = 2^2$
$= 4$

Q.2 $CH_3 - CH = CH - CH = CH - CH_3$

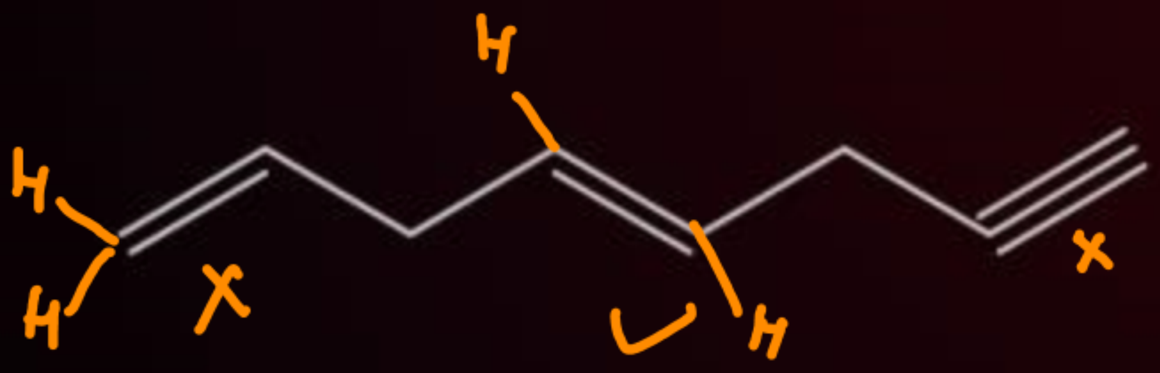
Symmetry

$n = 2$

$P = \frac{n}{2} = \frac{2}{2} = 1$

$TGI = 2^{n-1} + 2^{P-1}$
$= 2^{2-1} + 2^{1-1}$
$= 2^1 + 2^0$
$= 3$

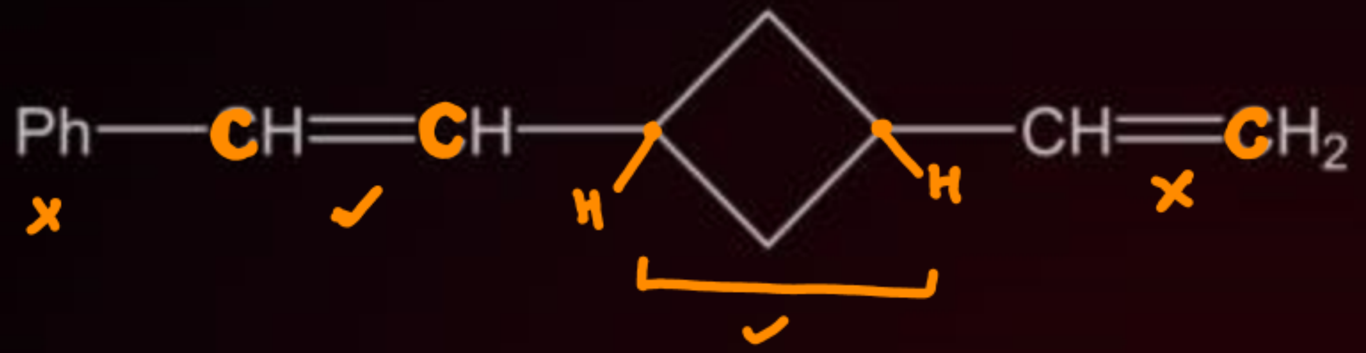
Q.3



Unsymmetry

$n = 1$

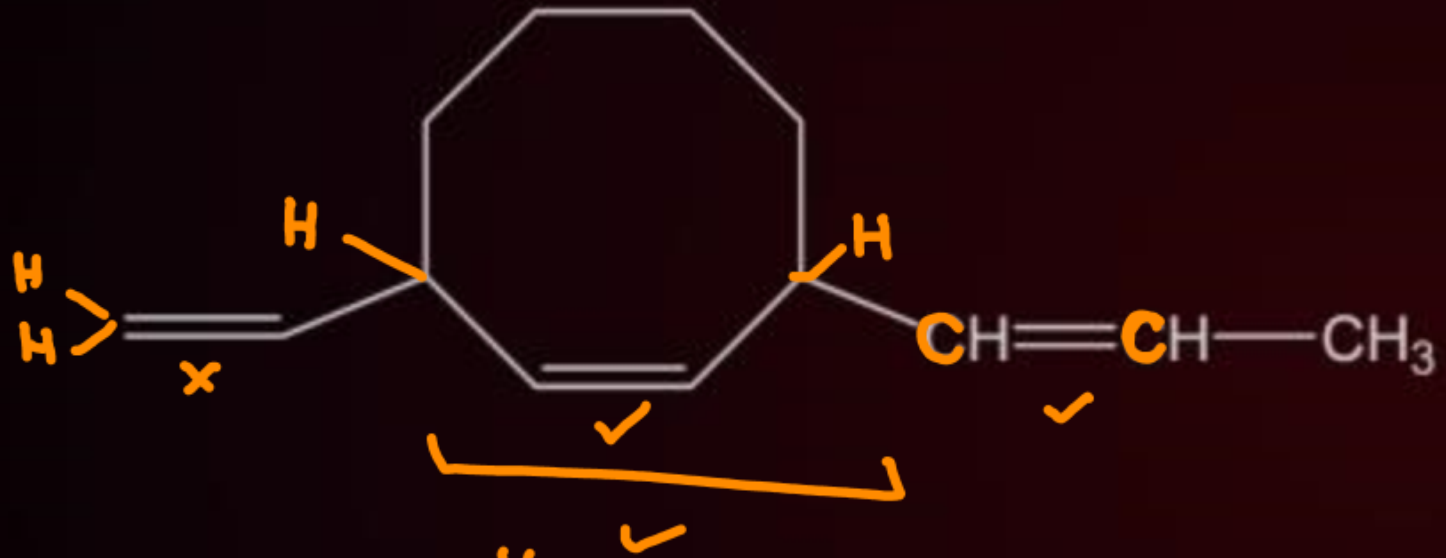
$TGI = 2^n$
$= 2^1 = 2$

Q4 

Unsymmetry

$n=2$

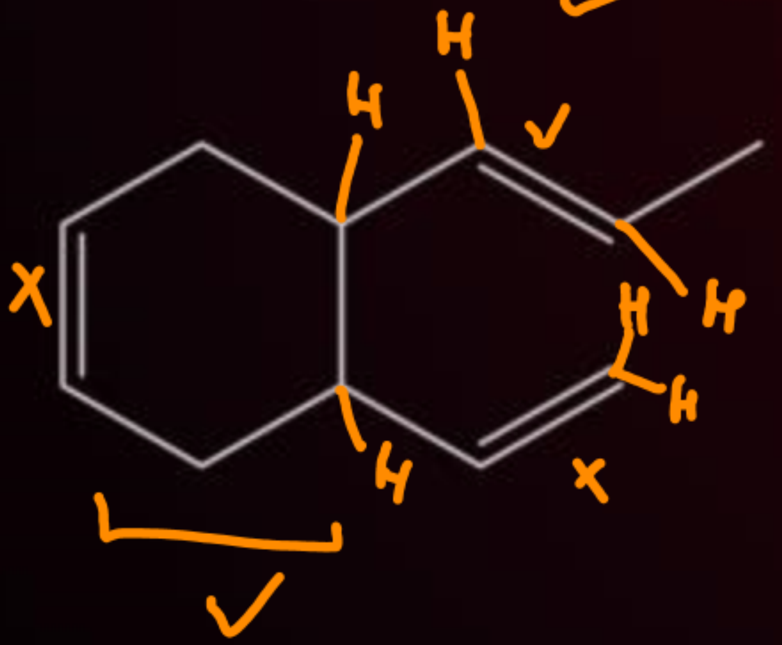
$TGI = 2^n = 2^2 = 4$

Q. 

Unsymmetry

$n=3$

$TGI = 2^n = 2^3 = 8$

Q. 

Unsymmetrical

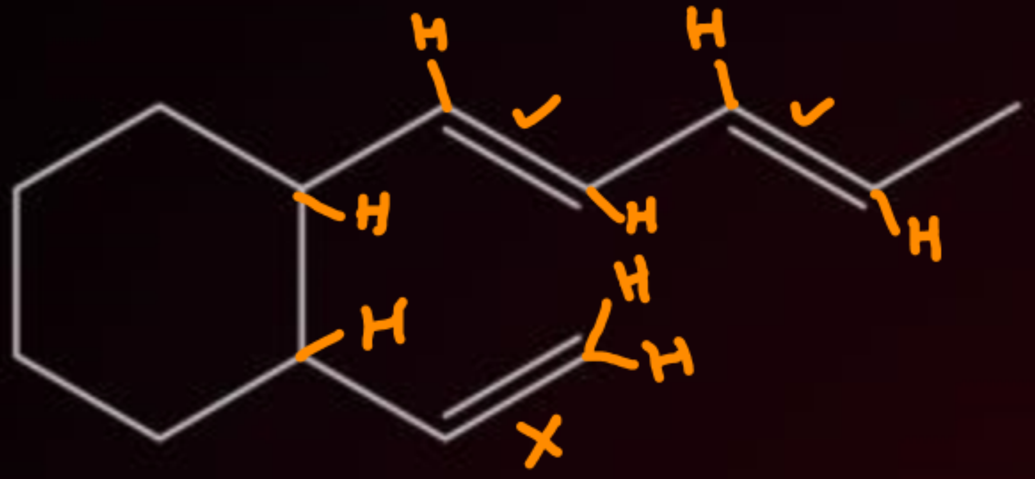
$n=2$

$TGI = 2^n$

$= 2^2$

$= 4$

Q.

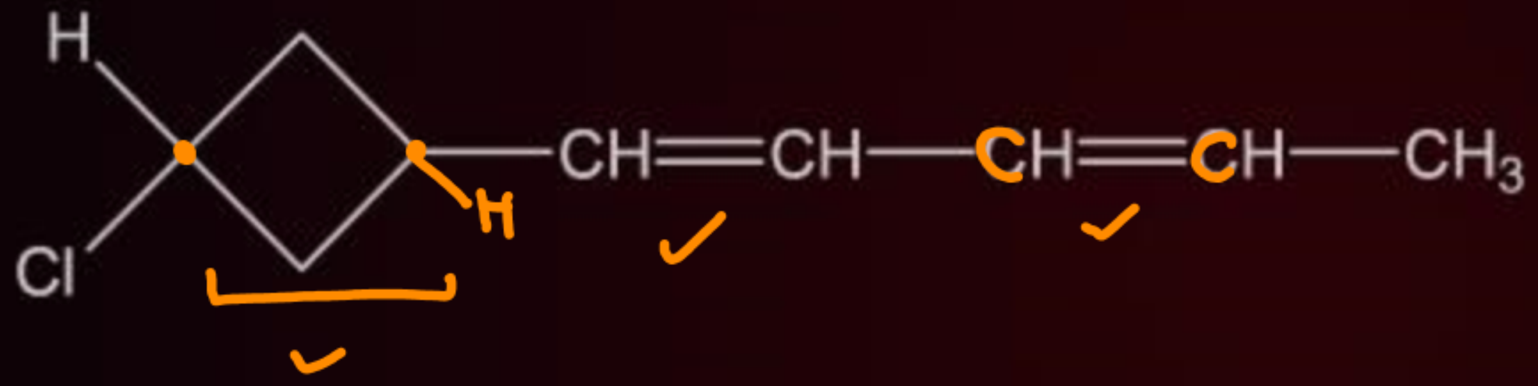


Unsymmetrical

$n = 3$

$TGI = 2^n$
$= 2^3$
$= 8$

Q.



Unsymmetrical

$n = 3 \quad TGI = 2^n = 2^3 = 8$

Q.



Unsymmetrical $\quad TGI = 2^n = 2^2 = 4$

$n = 2$

PYQ

Q. $CH_3 - CH = C(Br) - C(Br) = CH - CH_3$

Symmetrical

$n = 2$

$P = \frac{n}{2} = \frac{2}{2} = 1$

$TGI = 2^{n-1} + 2^{P-1}$

$= 2^{2-1} + 2^{1-1}$

$= 2^1 + 2^0$

$= 2 + 1 = 3$

PYQ

Q. $CH_2 = CH - CH = CH - CH = CH - CH = CH - CH = CH_2$

symmetrical

$n = 3$

$P = \frac{n+1}{2} = \frac{3+1}{2} = \frac{4}{2} = 2$

$TGI = 2^{n-1} + 2^{P-1}$

$= 2^{3-1} + 2^{2-1}$

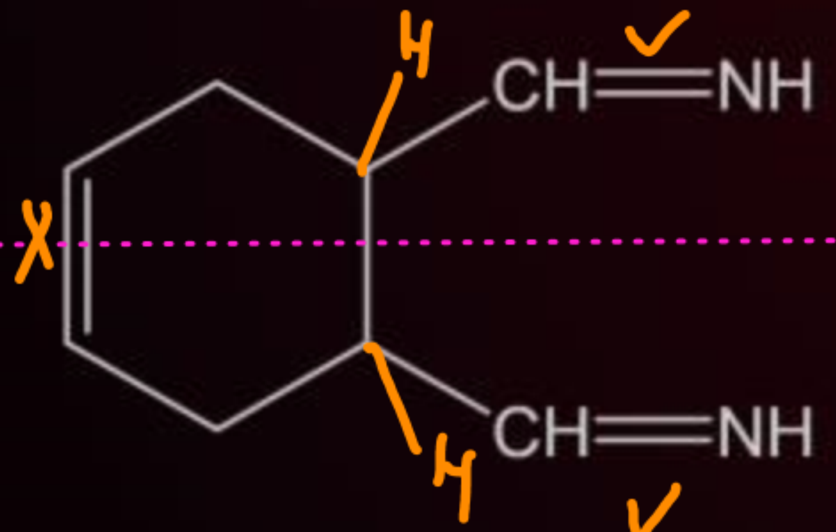
$= 2^2 + 2^1$

$= 4 + 2$

$= 6$

PYQ

Q.



Symmetrical

$n = 3$

$P = \frac{n+1}{2} = \frac{3+1}{2} = \frac{4}{2} = 2$

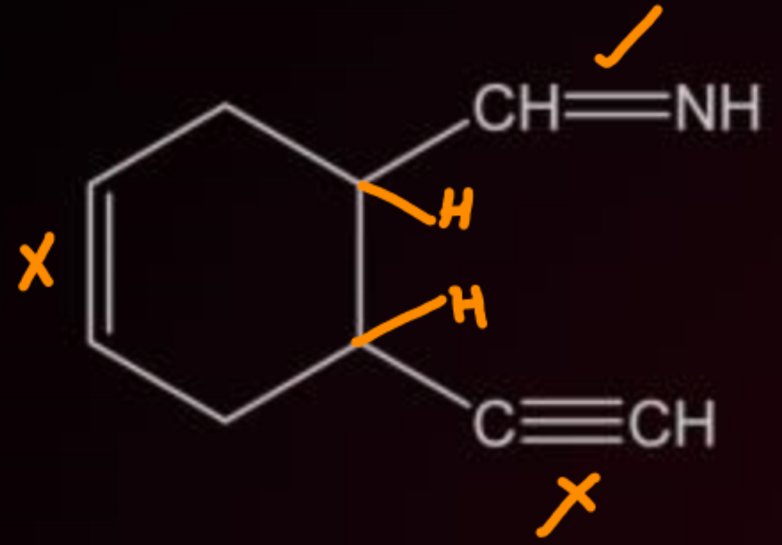
$TGI = 2^{n-1} + 2^{P-1}$

$= 2^{3-1} + 2^{2-1}$

$= 2^2 + 2^1$

$= 4 + 2 = 6$

Q.

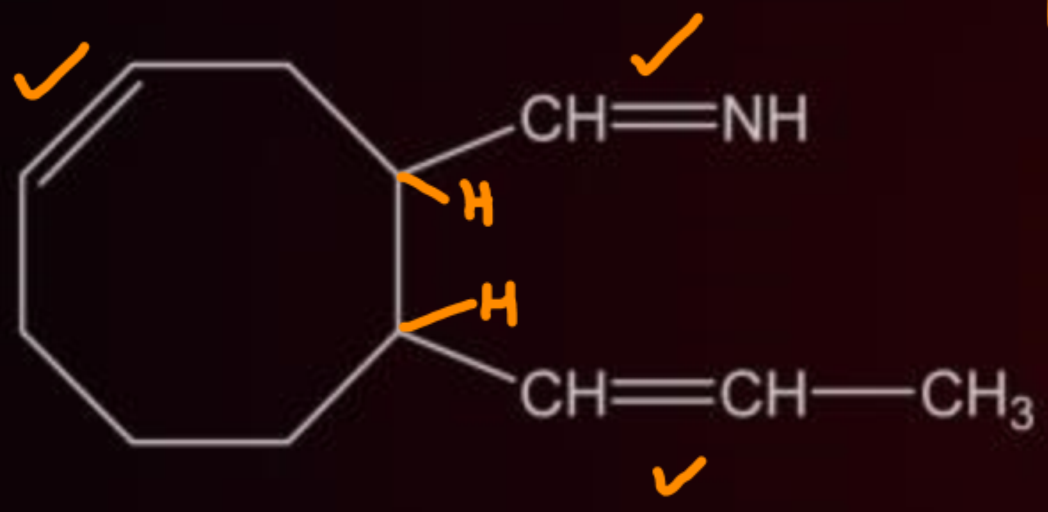


Unsymmetrical

$n = 2$

$TGI = 2^n = 2^2 = 4$

Q.

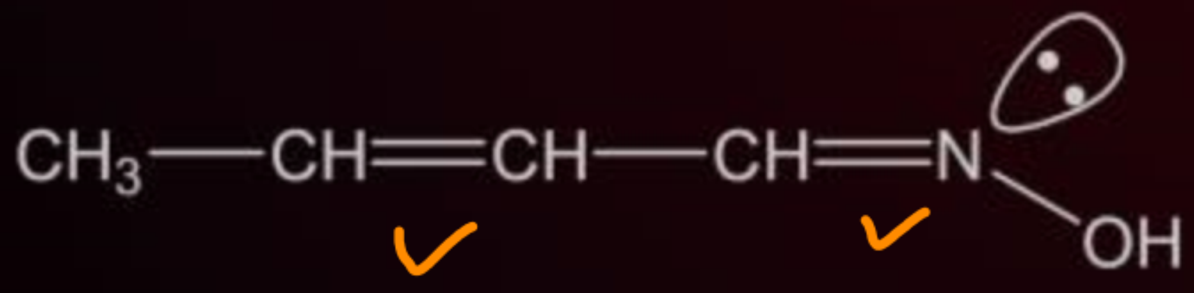


Unsymmetrical

$n = 4$

$TGI = 2^n = 2^4 = 16$

Q.



Unsymmetrical

$n = 2$

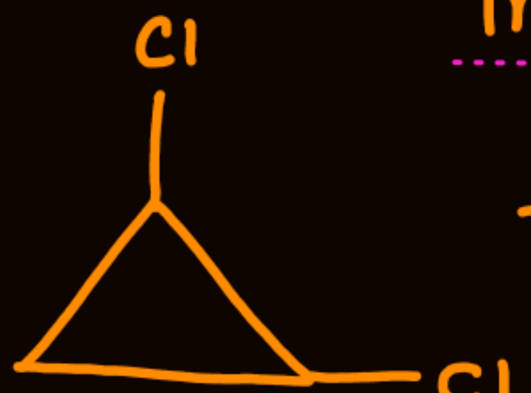
$TGI = 2^n$

$= 2^2$

$= 4$

In Some Cases Formula is not applicable

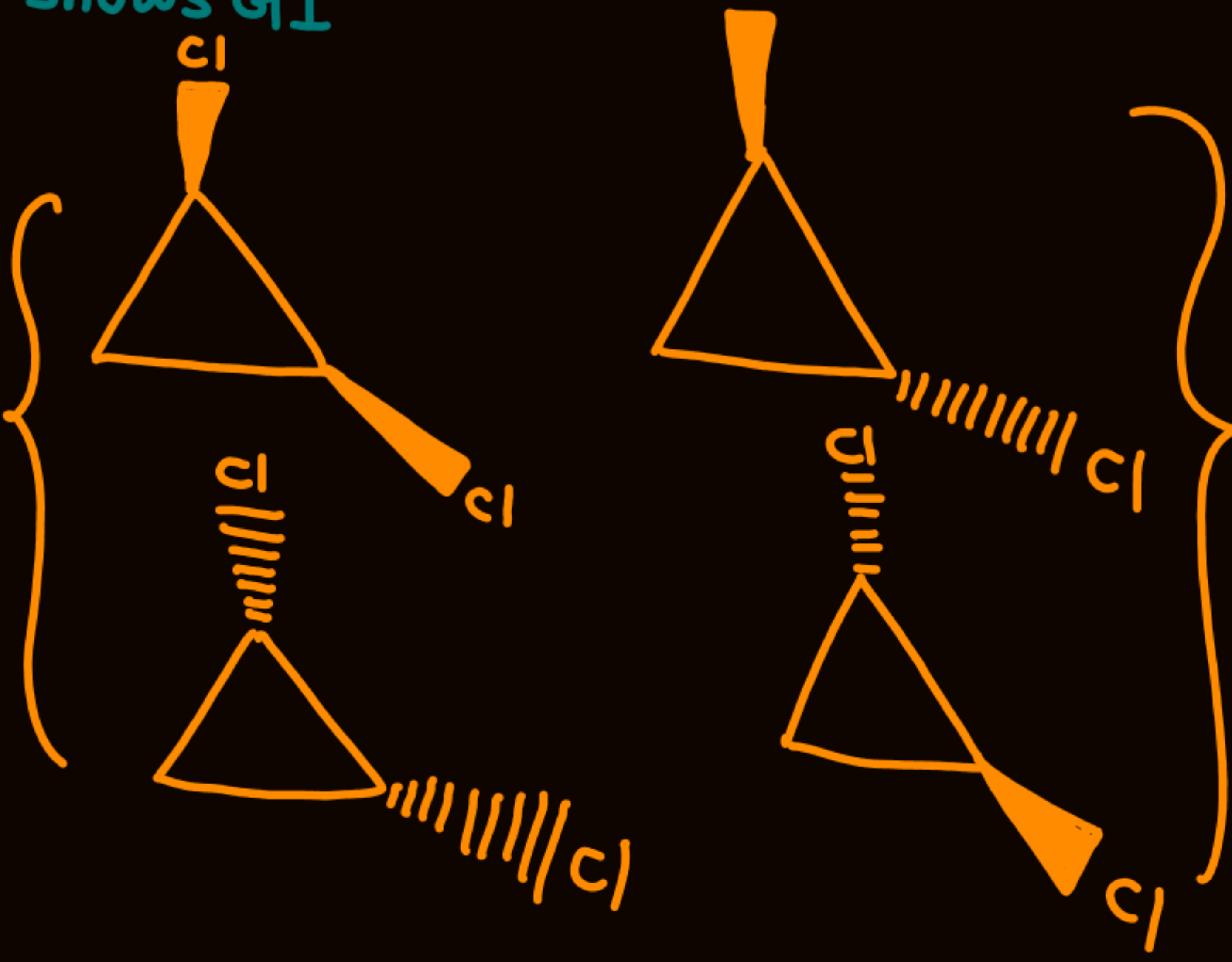
Case 1



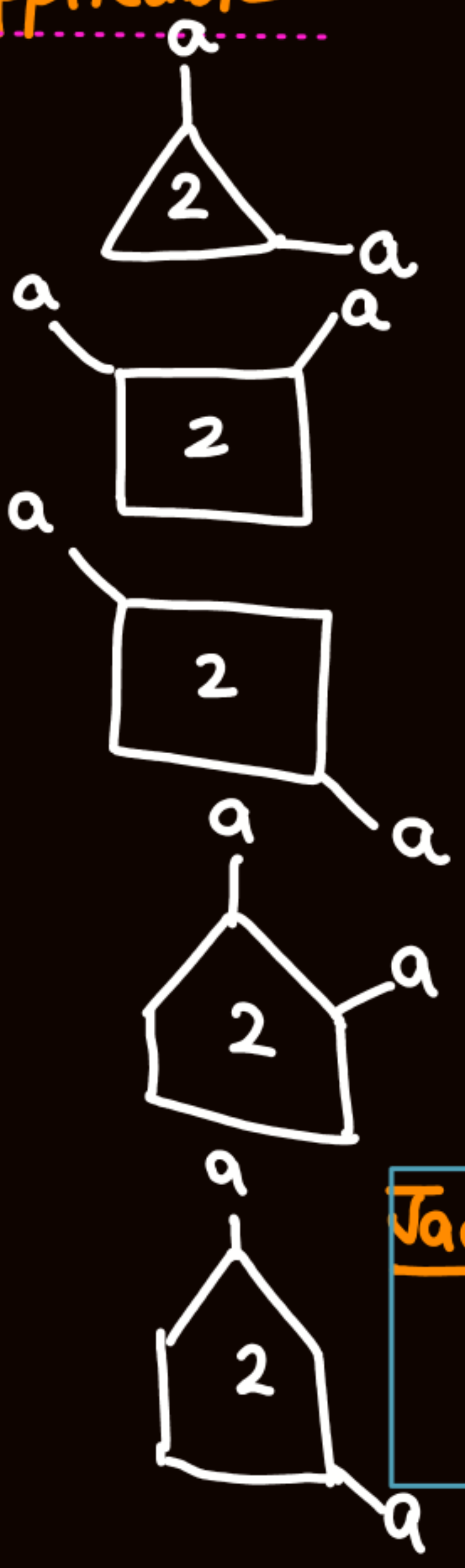
→ 2 GI

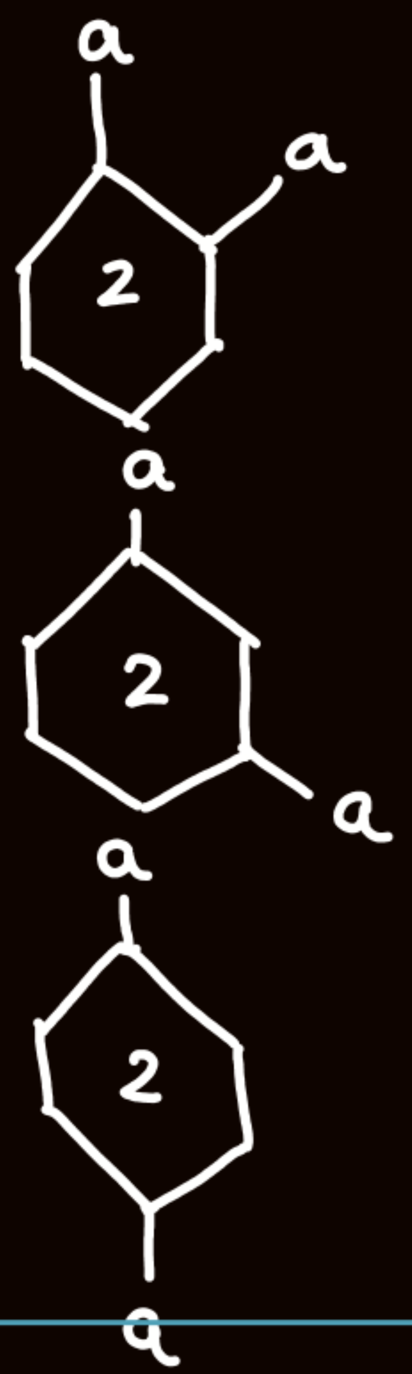
Shows GI

cys



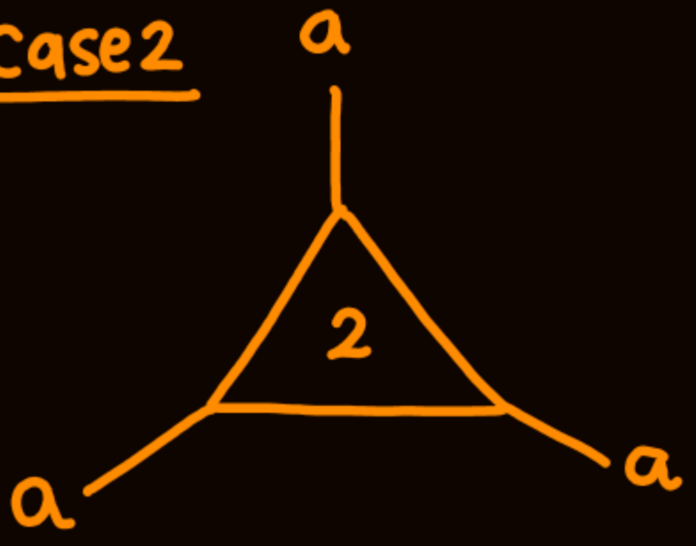
Trans



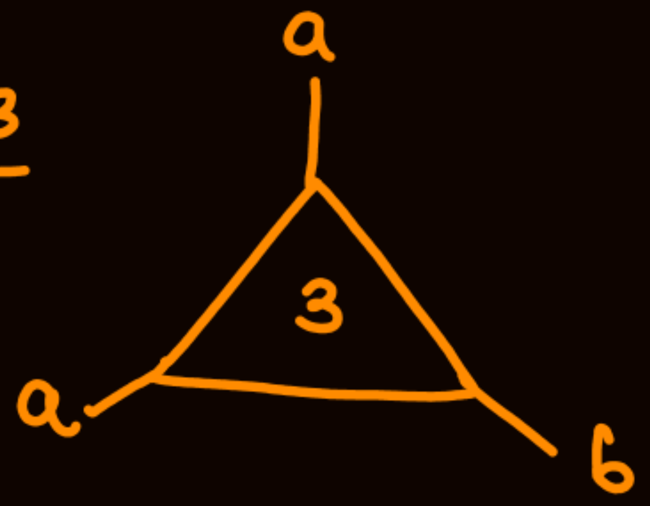


Jadu → diff grp + 1 = TGI

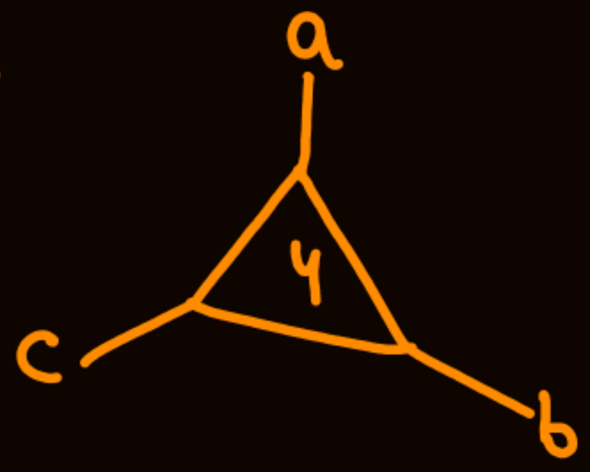
Case 2



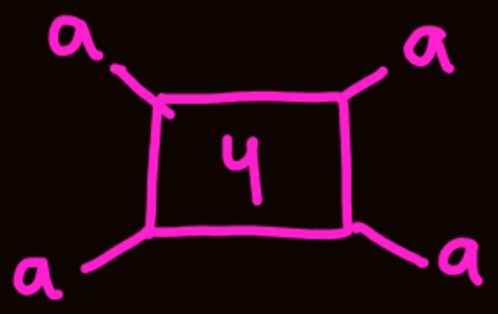
Case 3

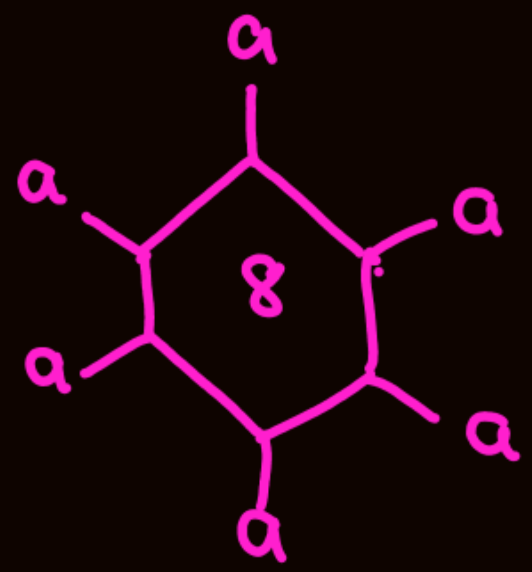


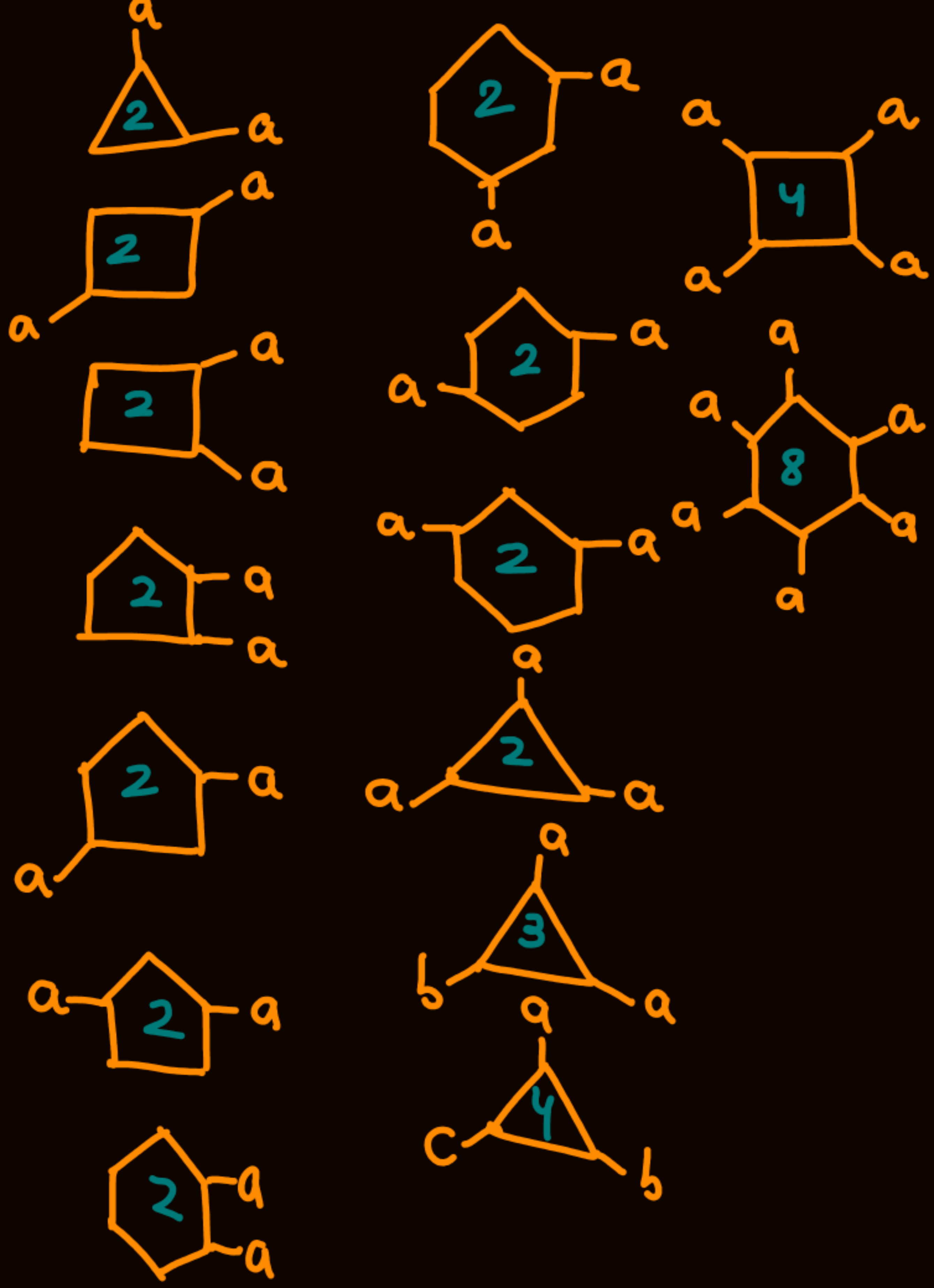
Case 4



कुछ case याद करना है।







PYQ

Q. Calculate Total G.I. in $C_6H_6Cl_6$.



8 GI

→ BHC
→ Benzene Hexa chloride
→ 6,6,6
→ Gammaxene
→ Lindane

} Powerful insecticide

Q. Calculate Total G.I. in $C_6H_6(CH_3)_6$ or $C_{12}H_{24}$. / Hexamethyl Benzene



8 GI

Counting of Total isomers — Structural + GI

Q Cal Total isomers in C_3H_6.

$DU = 4 - \frac{6}{2} = 4 - 3 = 1$

- cyclic → Ring
- acyclic → doublebond

Ring	doublebond
	C−C=C

Total isomer = 2 → Str + GI + OI

Total str isomer = 2

Total str cyclic isomer = 1

Total str acyclic isomer = 1

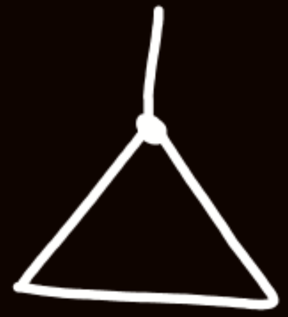
Total alkene = 1

Que Cal Total isomer in C_4H_8.

DU = 1
- cyclic → Ring
- acyclic → doublebond

cyclic/Ring





acyclic/openchain

C–C–C=C

C–C=C–C
- cys
- Trans

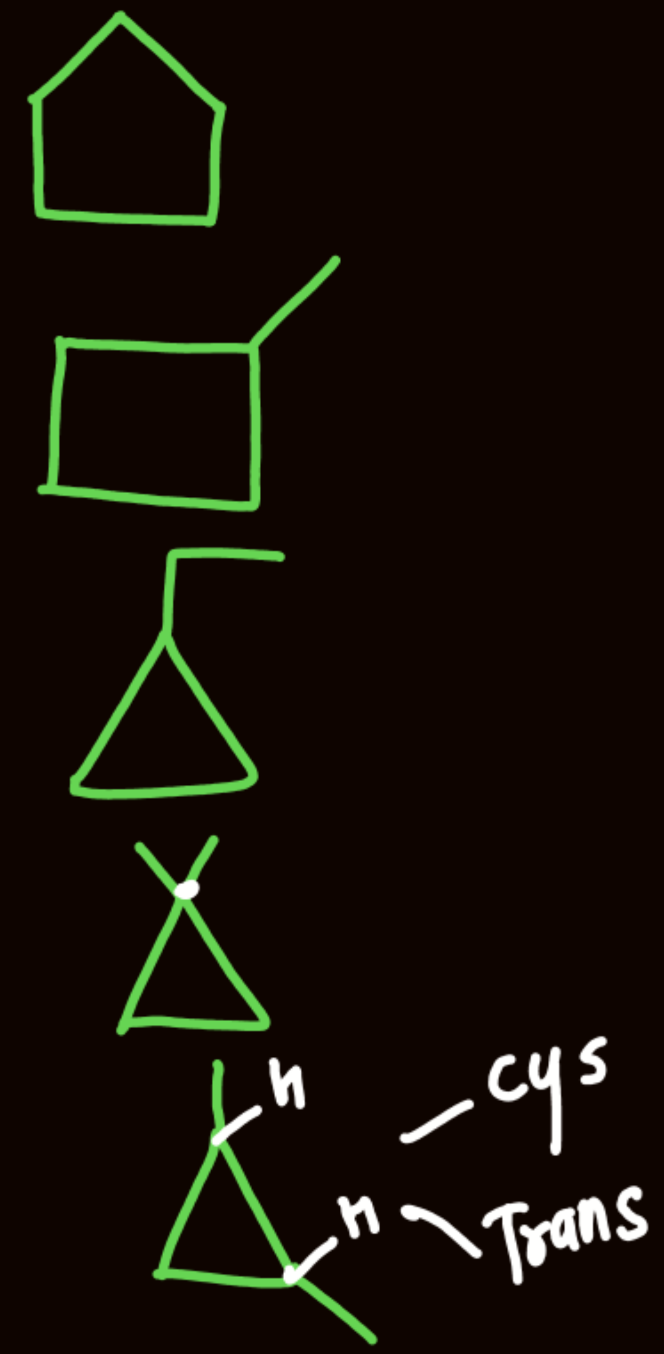


Total isomer = 6
Total str isomer = 5
Total GI = 2
Total alkene = 4
Total str cyclic isomer = 2
Total Geometrical cyclic isomer = 0
Total str acyclic isomer = 3
Total Geometrical acyclic isomer = 2

Que Cal Total isomer in C_5H_{10}

DU = 1

cyclic



acyclic

C–C–C–C=C

C–C–C=C–C — cys / Trans

```
C–C–C=C
    |
    C

C–C=C–C
    |
    C

C=C–C–C
    |
    C
```

Total isomer = 12

Total str isomer = 10

Total cyclic isomer = 6

Total str cyclic isomer = 5

Total acyclic isomer = 6

Total str acyclic isomer = 5

Total cyclic GI = 2

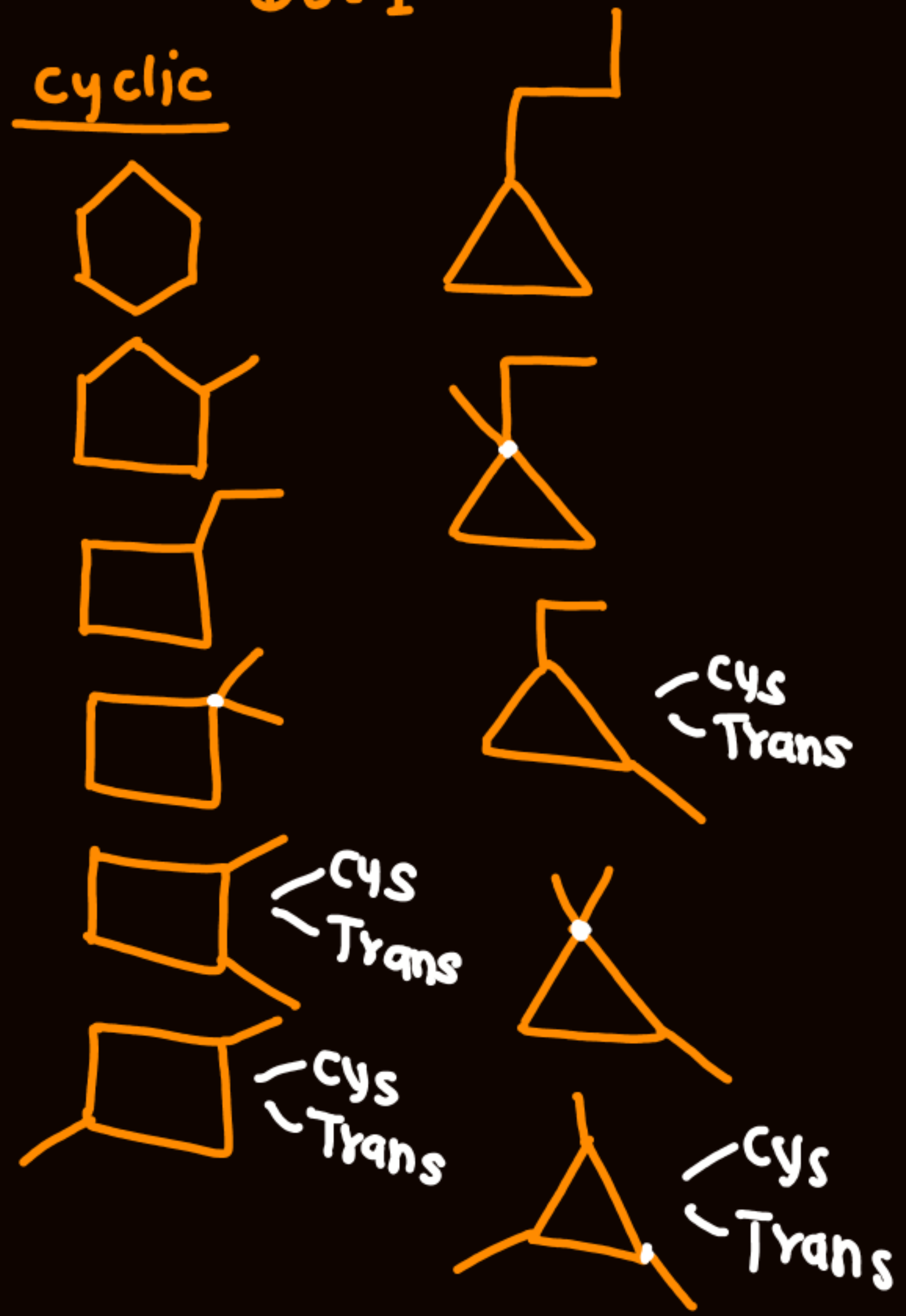
Total acyclic GI = 2

Total alkene = 6

Q Cal Total cyclic isomer in C_6H_{12}.

DU= 1

cyclic



Total isomer = 15

Total str cyclic isomer = 11

Total Gemetrical cyclic isomer = 8

OPTICAL Isomerism

Two or more comp having diff behaviour towards PPL are k/a optical isomers.

Polarimeter Experiment



Sunlight or Sodium lamp →



Vibrations in all directions →



nicol prism ↓ made of Calcite ↓ crystalline form of $CaCO_3$ →

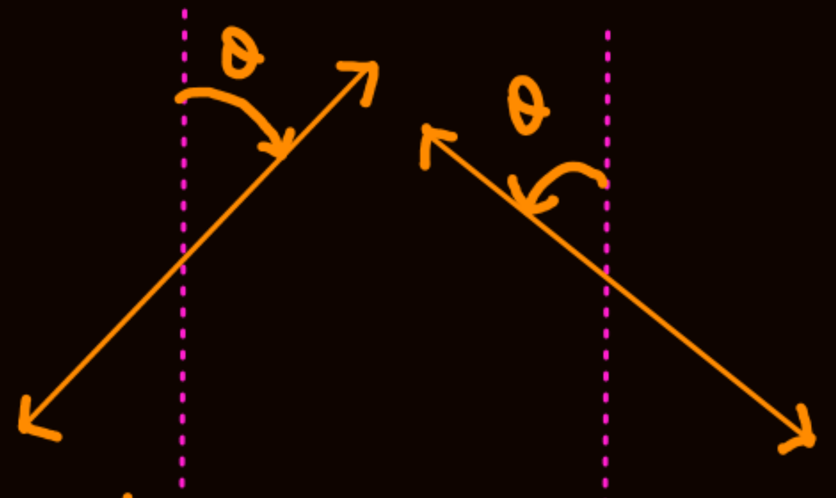
Plane Polarized Light (PPL) →

organic comp solution
↳ concentration = gm/cc (density) = gm/ml

Polarimeter tube

l (dm)

↓



θ angle clockwise — dextrorotatory — d — +

θ angle anticlockwise — leavorotatory — l — −

optically inactive

'θ' (angle of rotation) depends on —

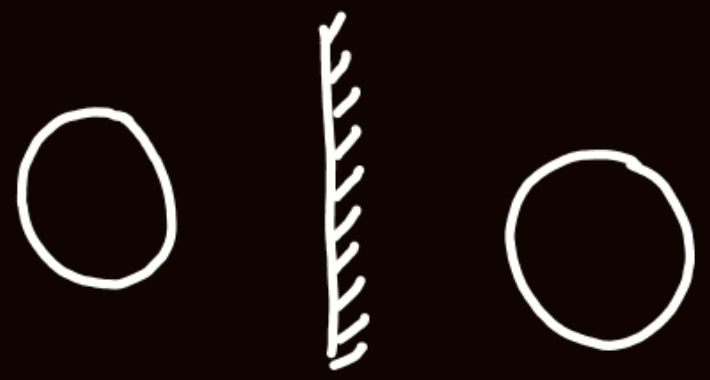
1. Length of polarimeter tube / Path length
2. nature of Substance (solute)
3. Types of Solvent
4. Concentration of OC → gm/cc or gm/ml
5. Temp
6. Wavelength of light source

THANK YOU
All the Best!!

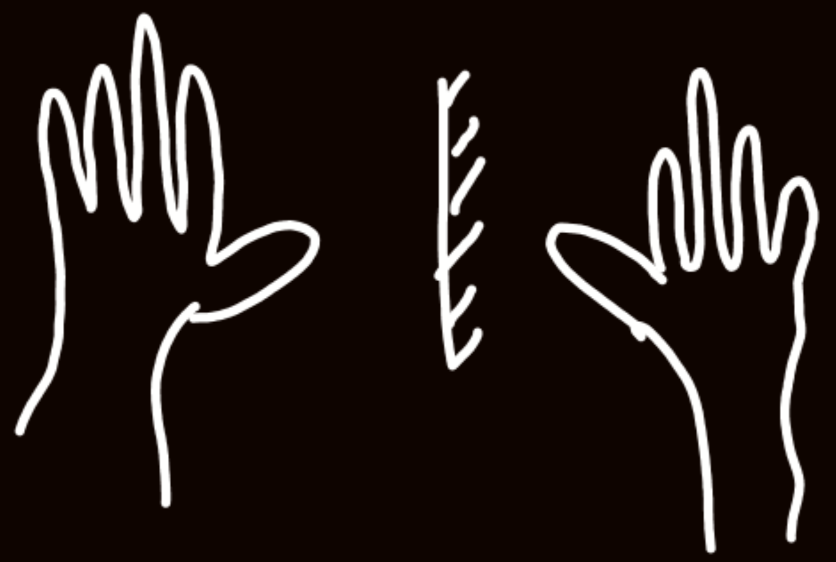
Condition to show optical isomerism

① chiral comp → Unsymmetrical → optically active] PPL rotates cw/ACW
achiral comp → Symmetrical → optically inactive] PPL donot rotates.

② Compound should have non-superimposable mirror image.



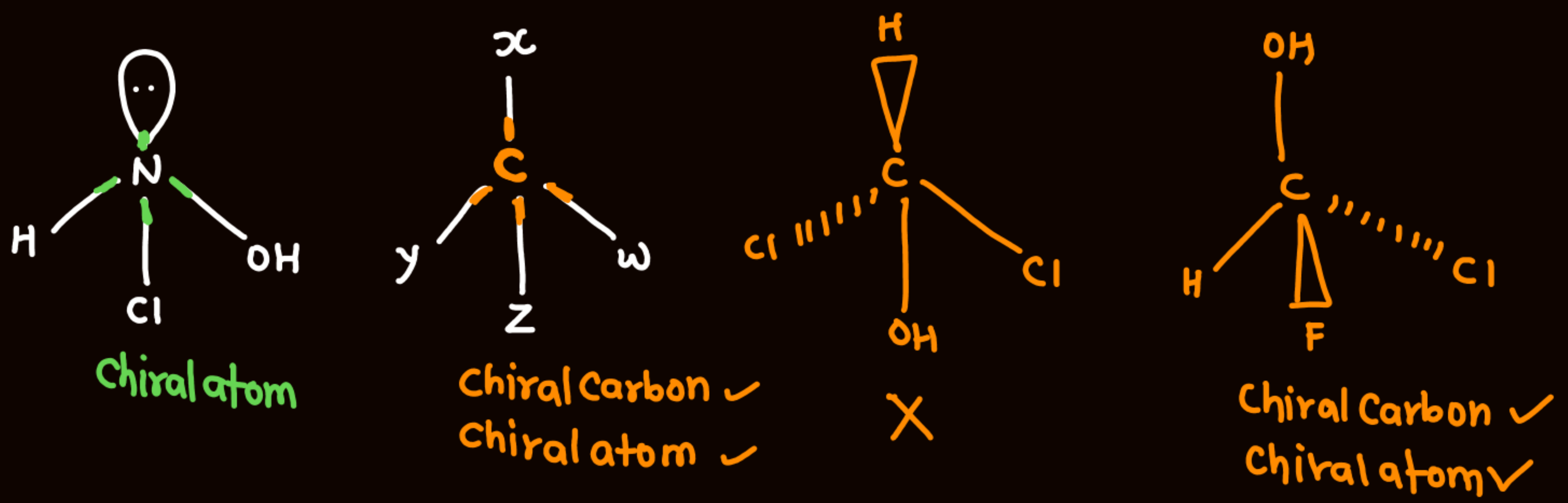
{ Superimposable Mirror Image } optically inactive



{ non Superimposable Mirror Image { optically active

Chiral center → Sp^3 atom having all 4 diff atom/group attatched is k/a chiral center.

Chiral Carbon → sp^3 Carbon " " " " " " Chiral Carbon.

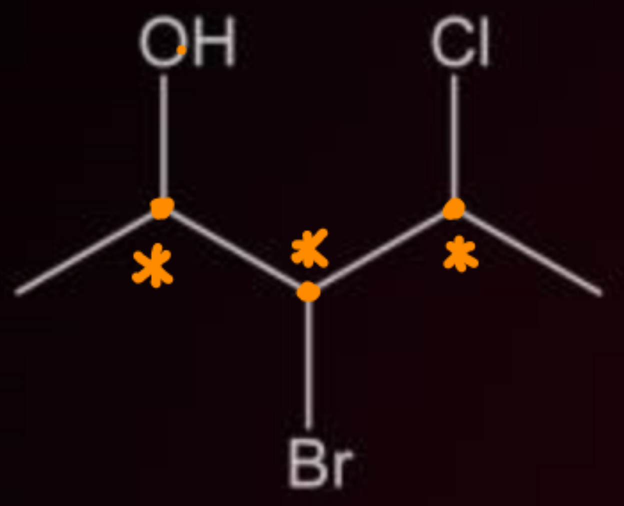


Q. Find number of chiral centers:

(1) $CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{*}{C}}H-CH_2-CH_3$

(2) $CH_3-\overset{\overset{\displaystyle Me}{|}}{C}H-\overset{\overset{\displaystyle Cl}{|}}{\underset{*}{C}}H-CH_3$

(3)



Chiralatom = 3

Chiral center = 3

Chiral carbon = 3

(4)

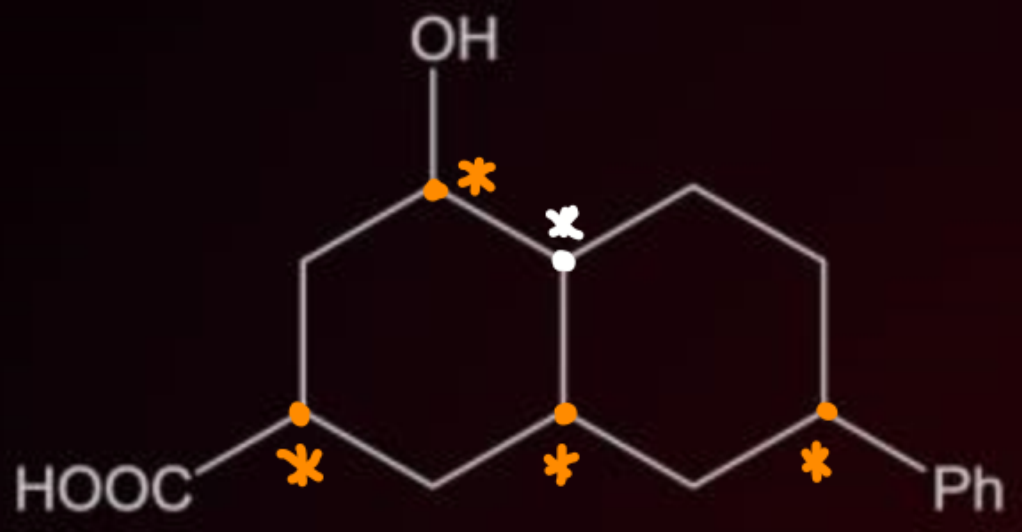


Chiral carbon = 2

" center = 2

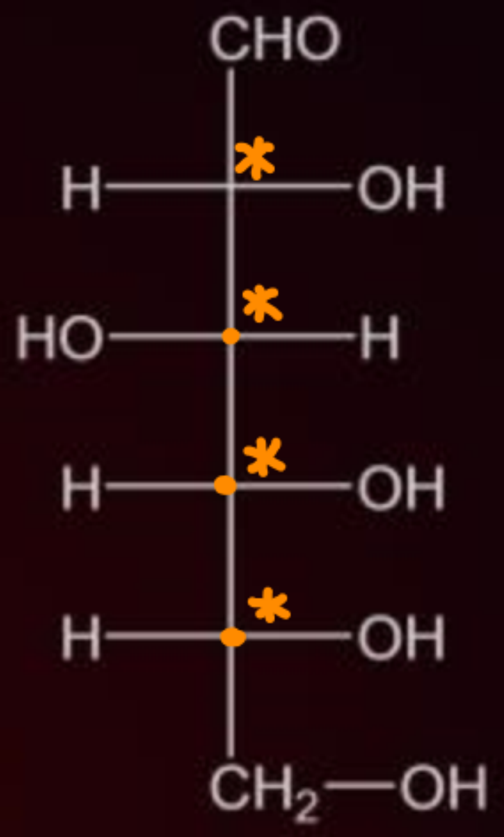
" atom = 2

(5)



Chiral carbon=5

(6)



4 chiral center.
4 chiral atom.
4 chiral carbon.

D-Glucose

acyclic

(7)



D-Glucose (cyclic)

5 Chiral Carbon

(8)

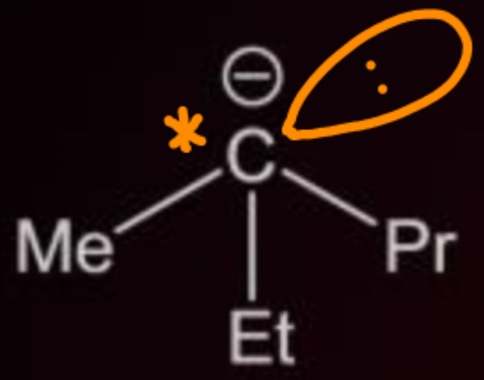


chiral carbon = 1

chiral atom = 2

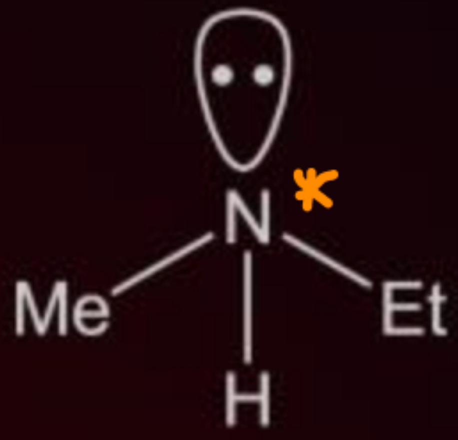
Chiral center = 2

(9)



Chiral Carbon = 1

(10)



Chiral Carbon = 0

" atom = 1

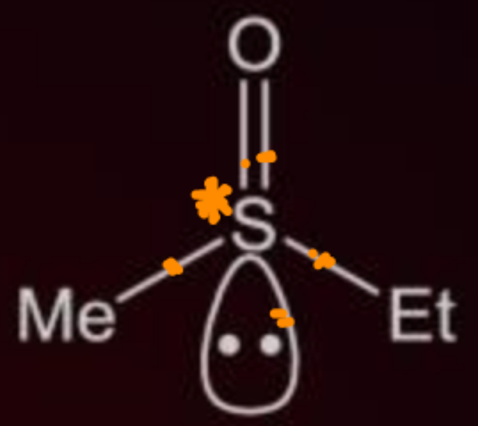
" Center = 1

(11)



Chiral Carbon = 0
atom = 1
Center = 1

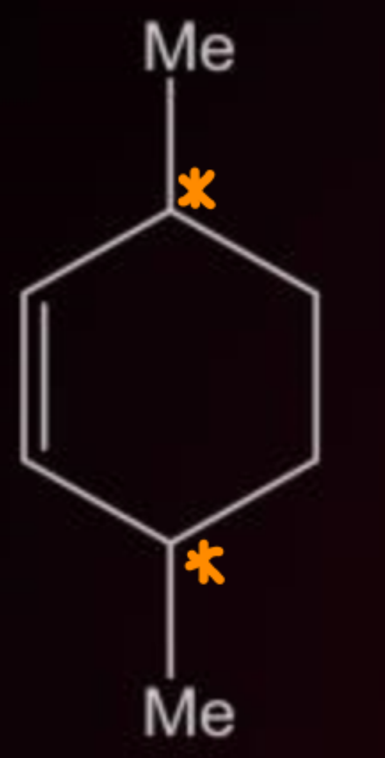
(12)



$\sigma + lp = 4$
$3 + 1 = 4$
↓
sp^3

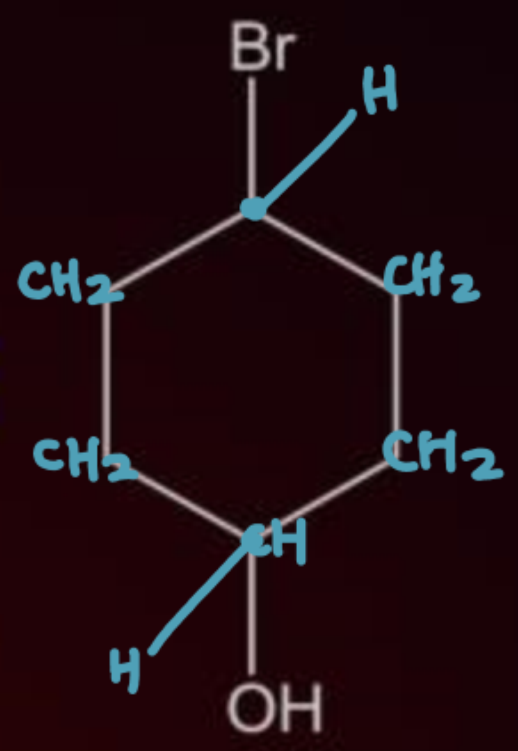
Chiral carbon = 0
atom = 1
Center = 1

(13)

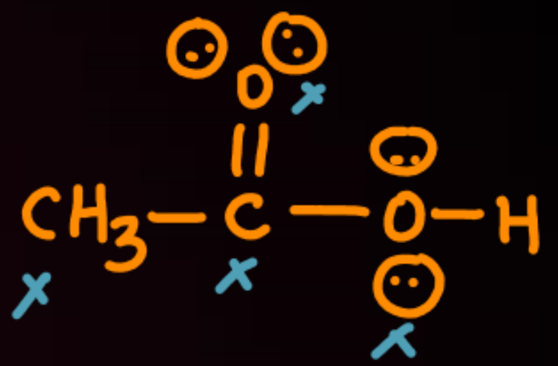


Chiral carbon = 2
" atom = 2
" Center = 2

(14)



Chircal carbon = 0
atom = 0
Center = 0

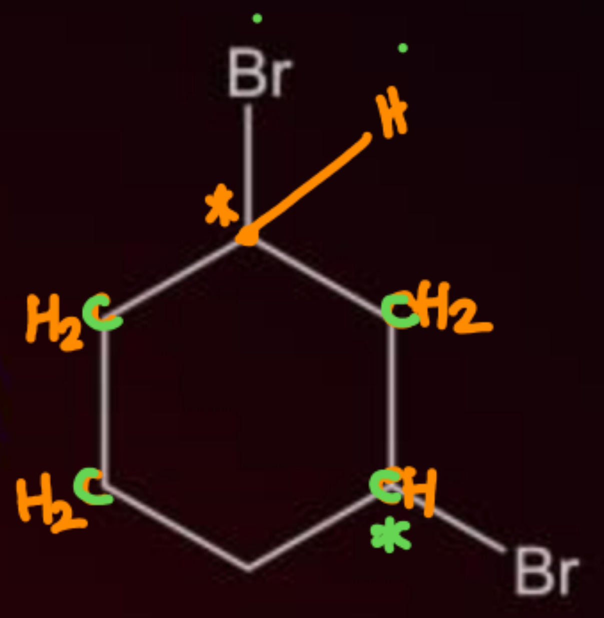


(15)



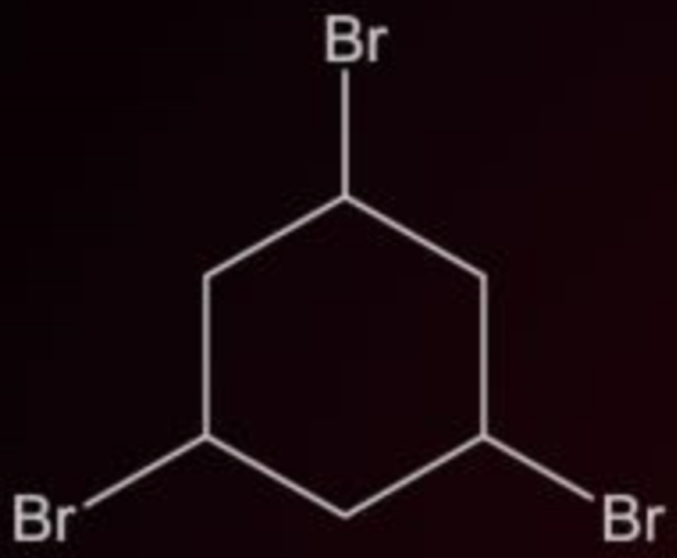
Chiral carbon = 0
atom = 0
center = 0

(16)



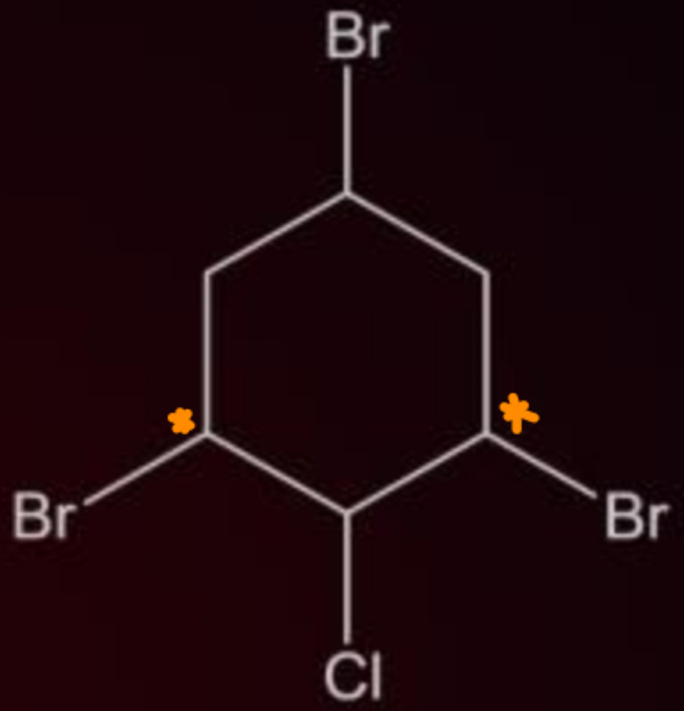
Chiral carbon = 2

(17)



Chiral carbon = 0
atom = 0
Center = 0

(18)



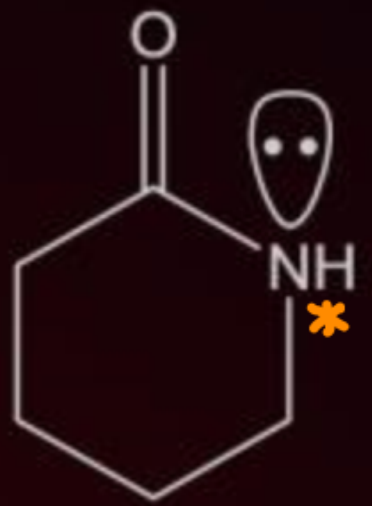
Chiral carbon = 2
atom = 2
Center = 2

(19)



Chiral Carbon = 4

(20)



Chiral carbon = 0
atom = 1
center = 1

note →

Note: Presence or absence of chiral carbon is not necessary condition for optical activity. The necessary condition for optical activity is absence of element of symmetry.

Elements of Symmetry

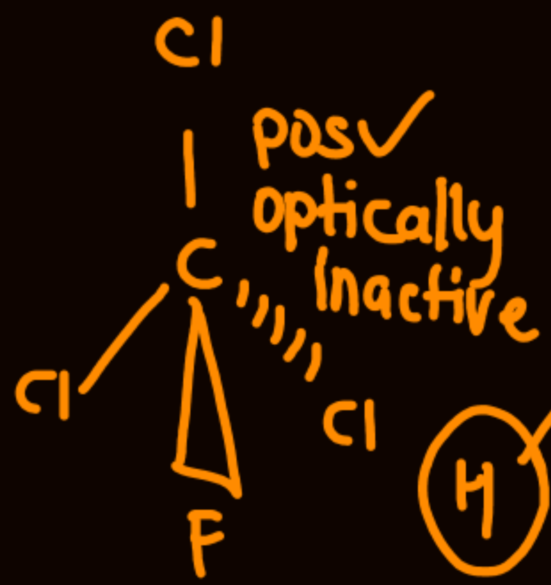
① Plane of Symmetry (POS)
② Center of Symmetry (COS)

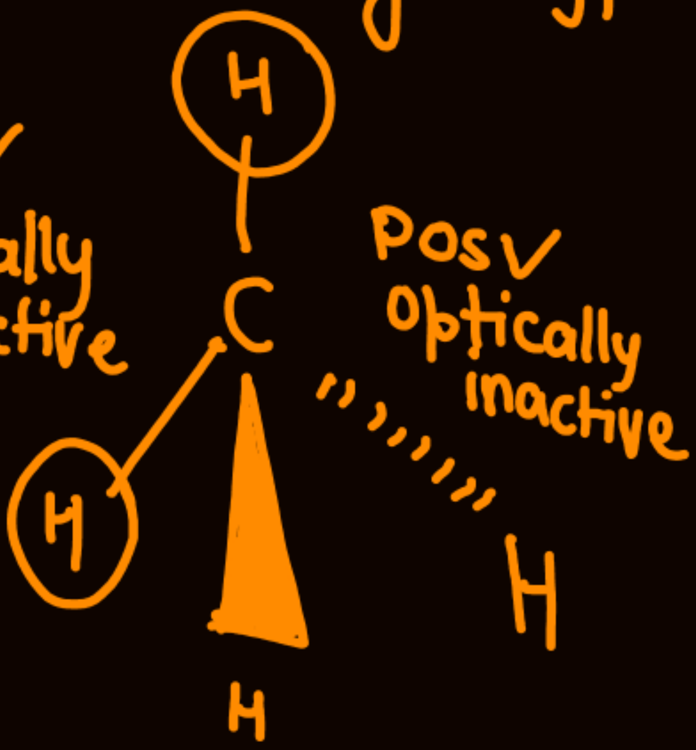
} syllabus

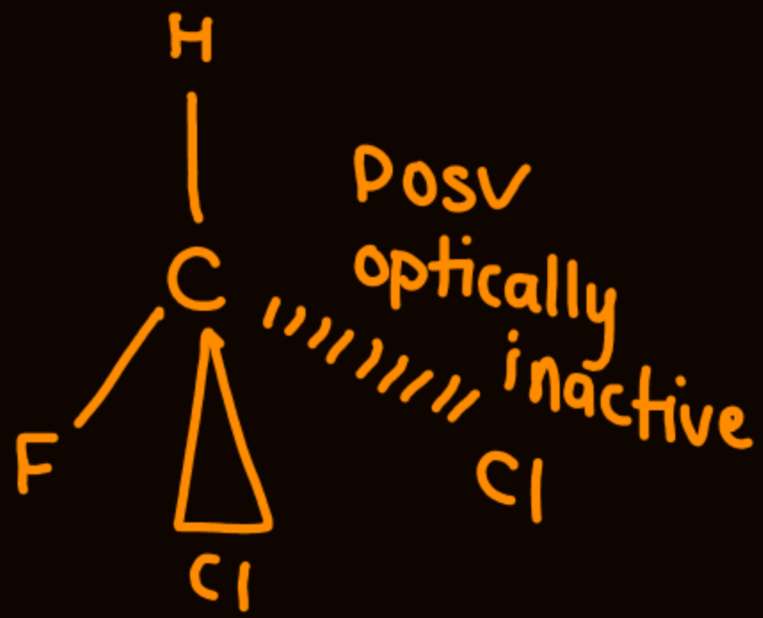
Plane of Symmetry (POS)

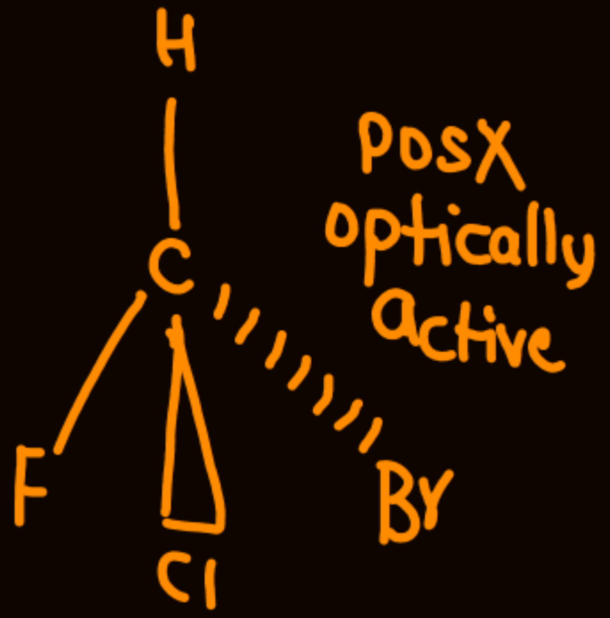
- * If POS is present → Comp is Symmetrical → optically inactive.
- * If POS is absent → Comp is unsymmetrical → optically active.

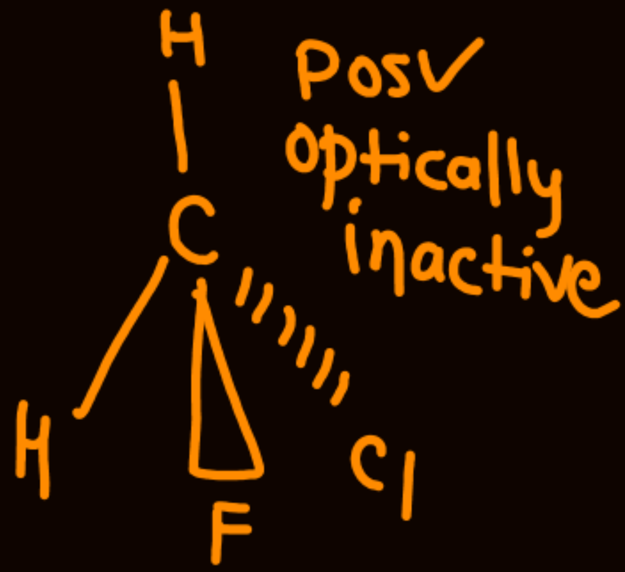
POS → Imaginary plane which divides molecule into two equal parts is k/a POS.



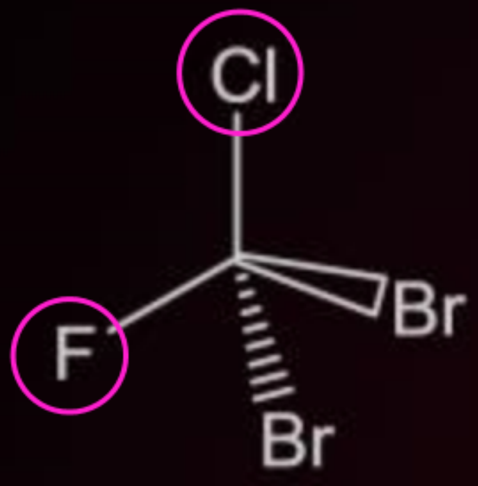








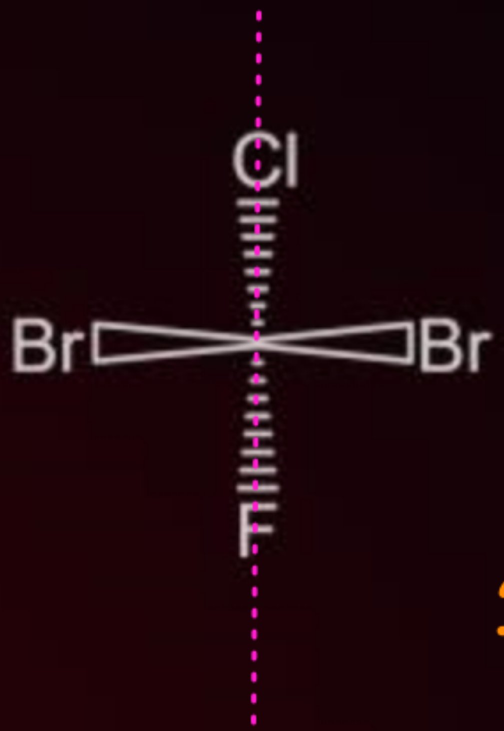
(1)



Pos ✓

Inactive

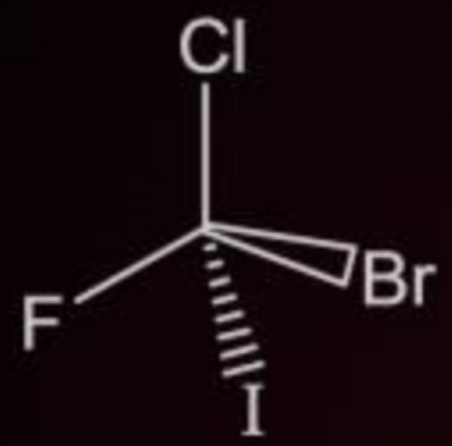
(2)



Pos ✓

Inactive ✓

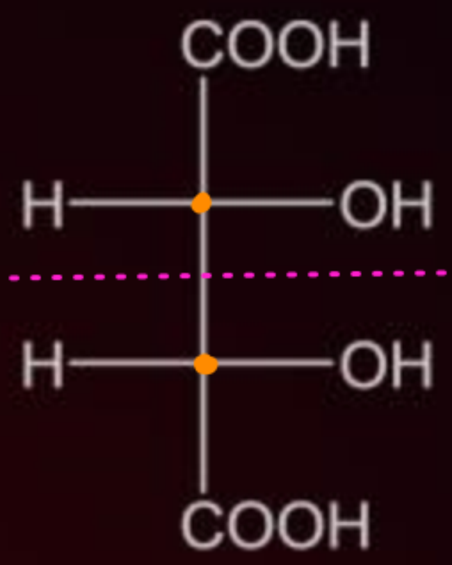
(3)



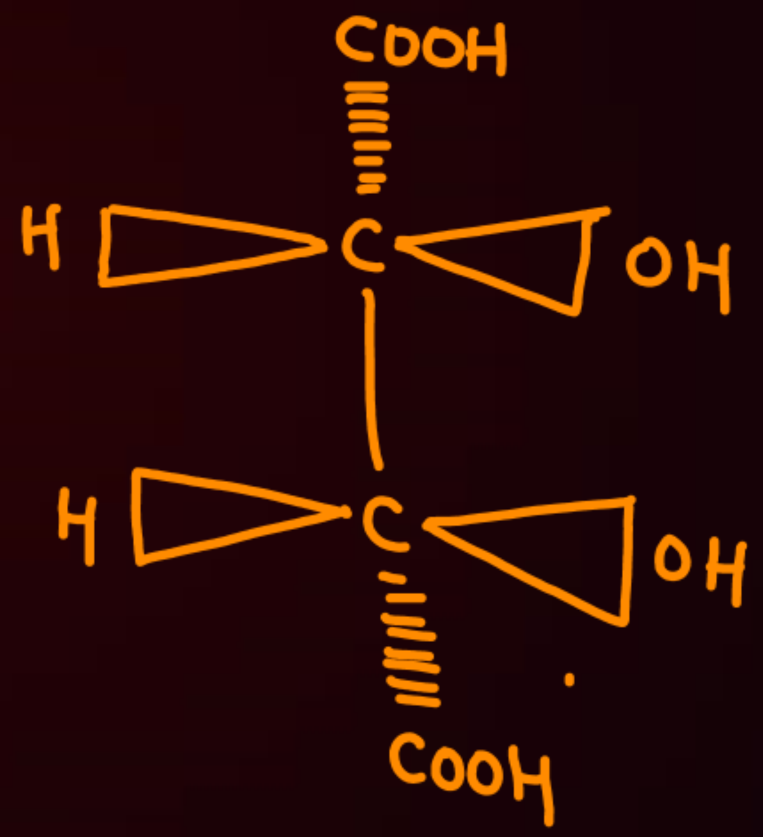
Pos ✗
active

(4)

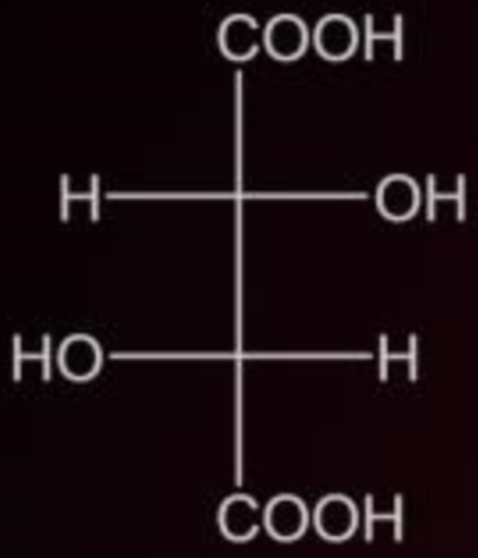
Hw
Vq



Pos ✓
Inactive ✓



(5)



Pos ✗
active

(6)



Pos ✓
Inactive

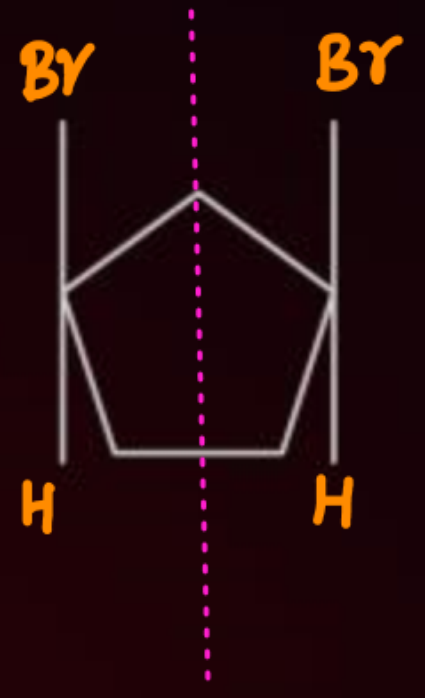
(7)



Pos ✗

active ✓

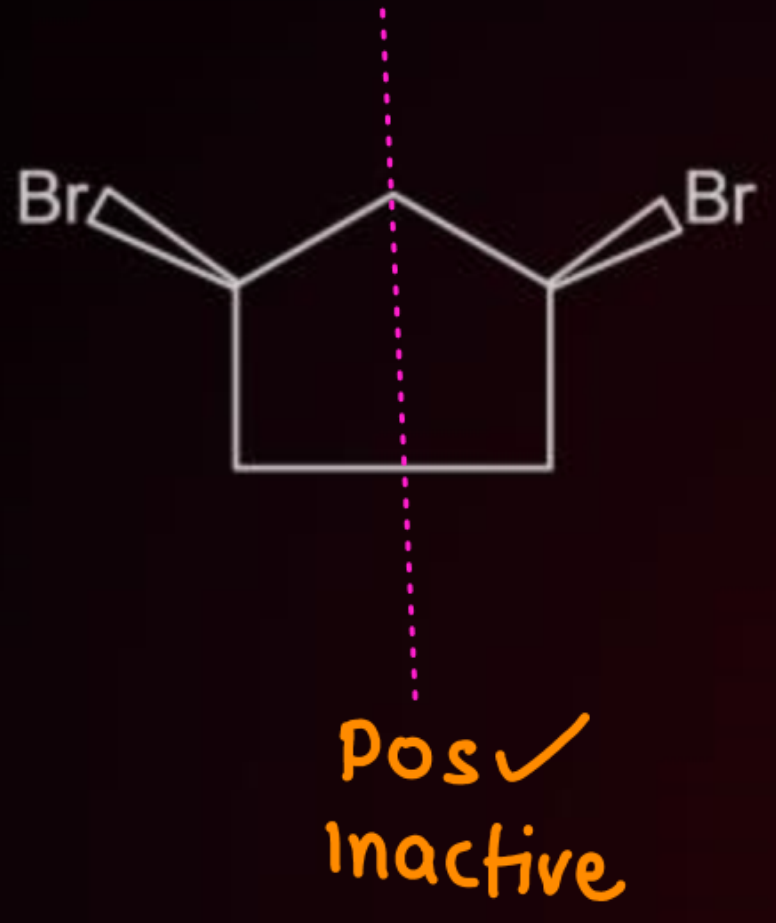
(8)



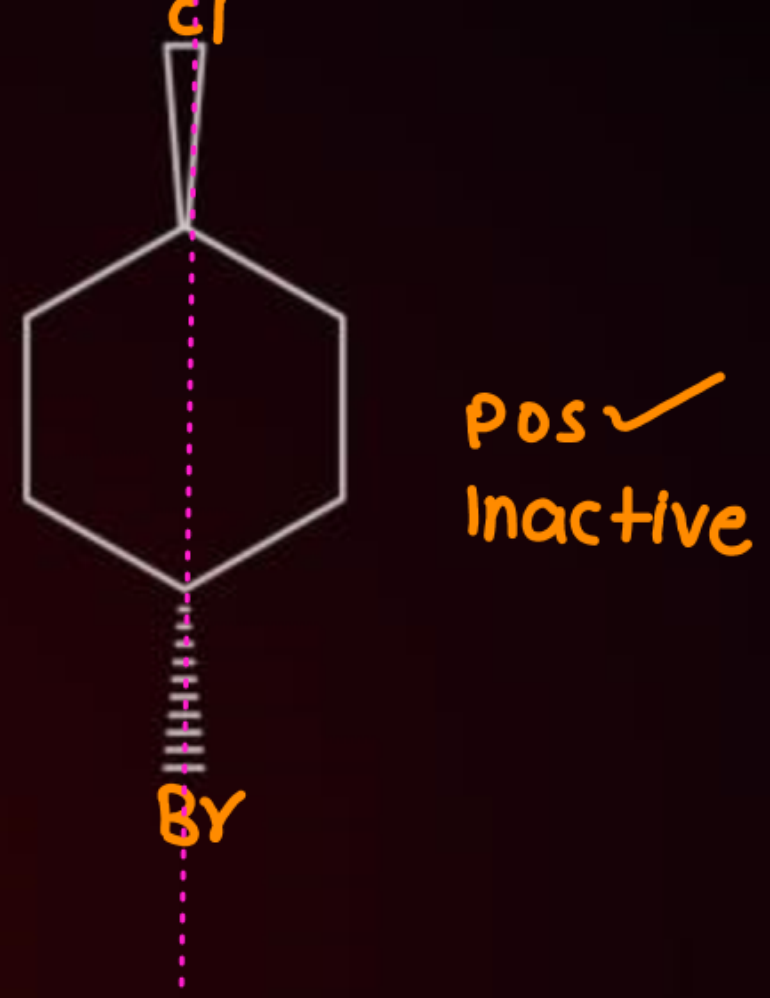
Pos ✓

Inactive

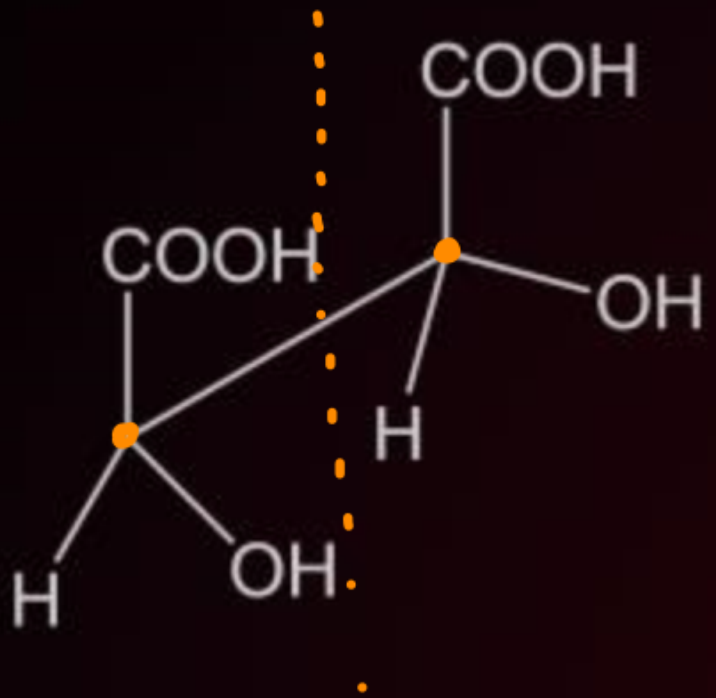
(9)



(10)

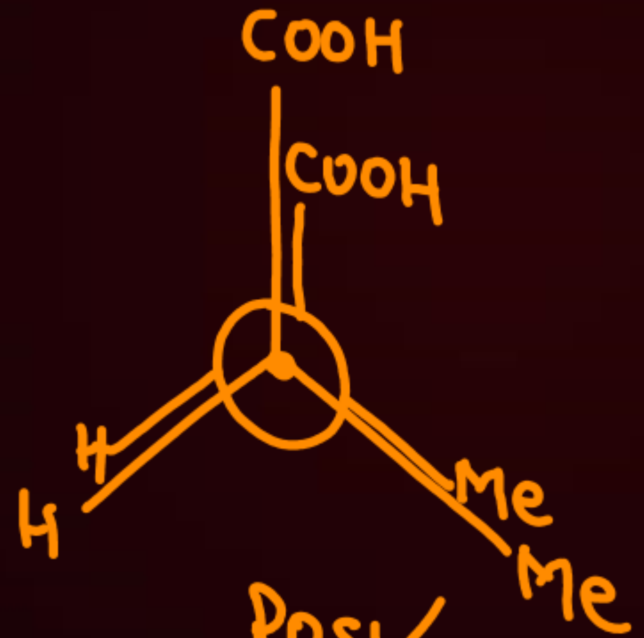


(11)



Pos ✓

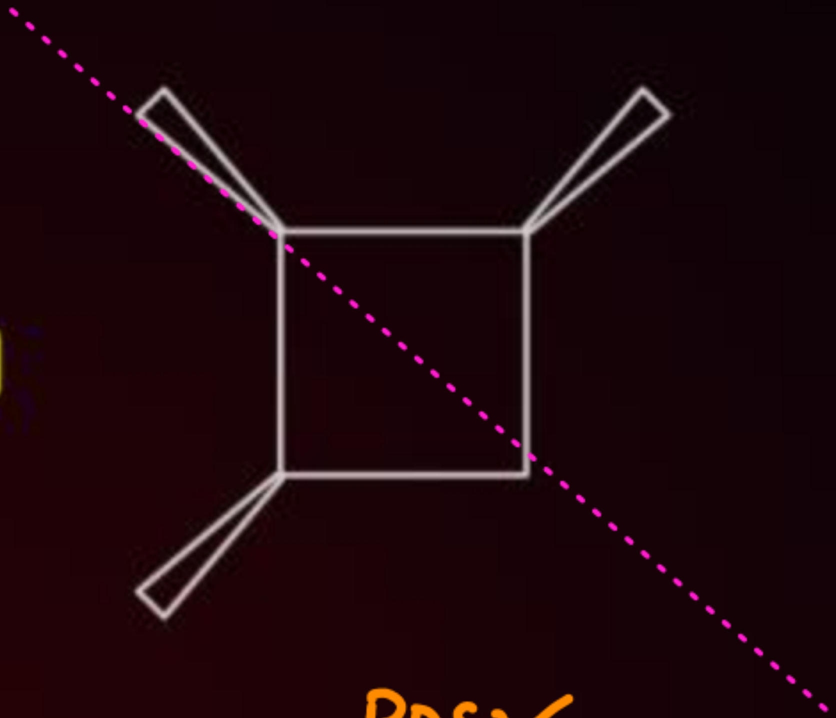
Inactive



Pos ✓

Inactive

(12)



Pos ✓

Inactive



Pos ✗

active

Center of Symmetry (COS)

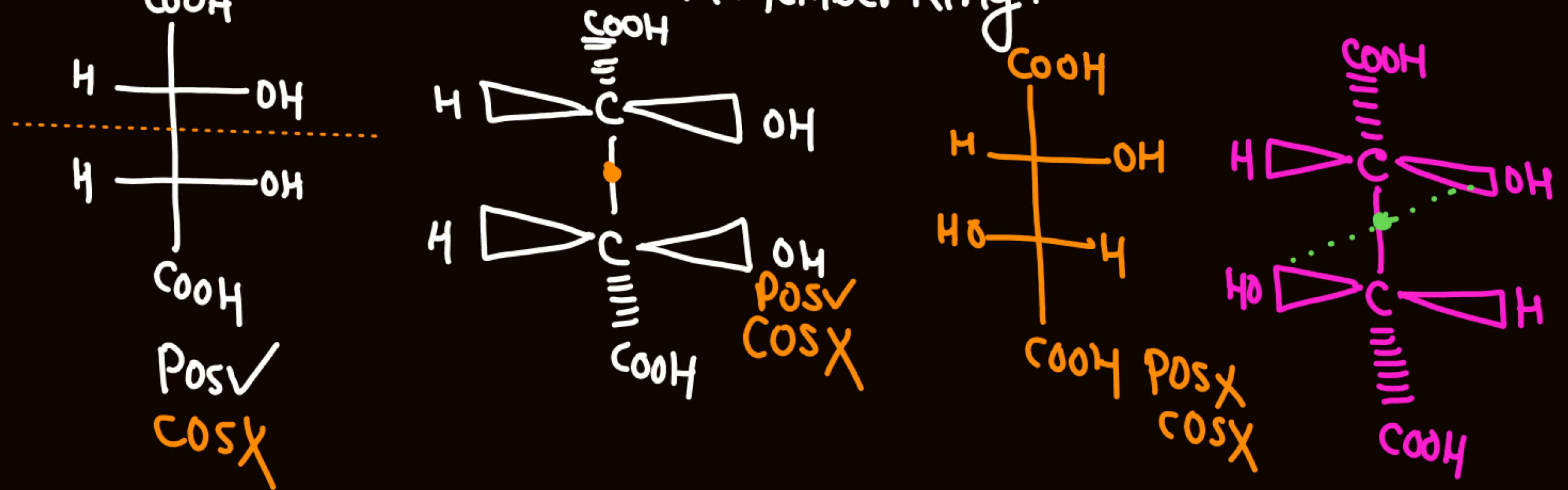
It is a point at Center of molecule from which if we go in equal & opposite direction we get same atom/group.



There is no cos in Fischer.

note → There is no COS in odd member Ring.

HW



(1) 

cos ✗

(2) 

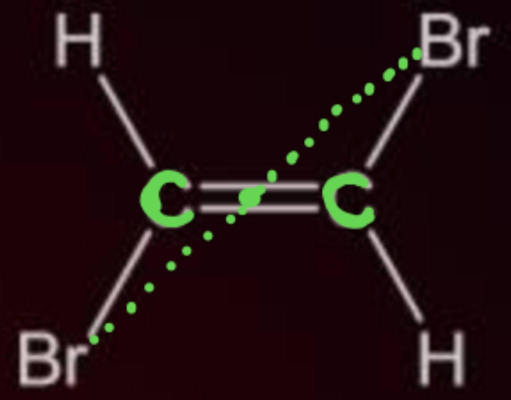
cos ✓

(3)



Cos✓

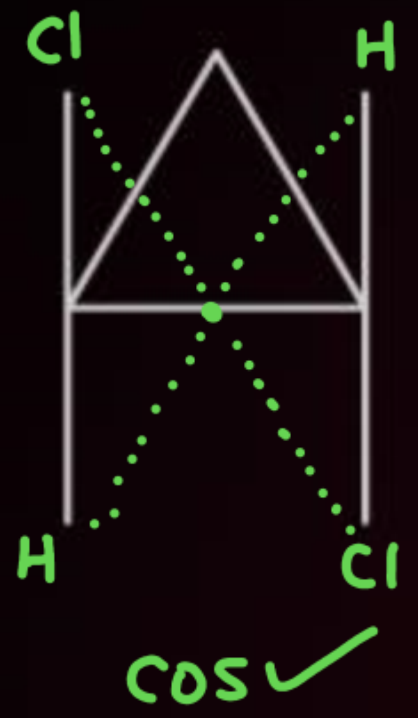
(4)



cos✓

Slicepos ✓

(5)



(6)



(7)



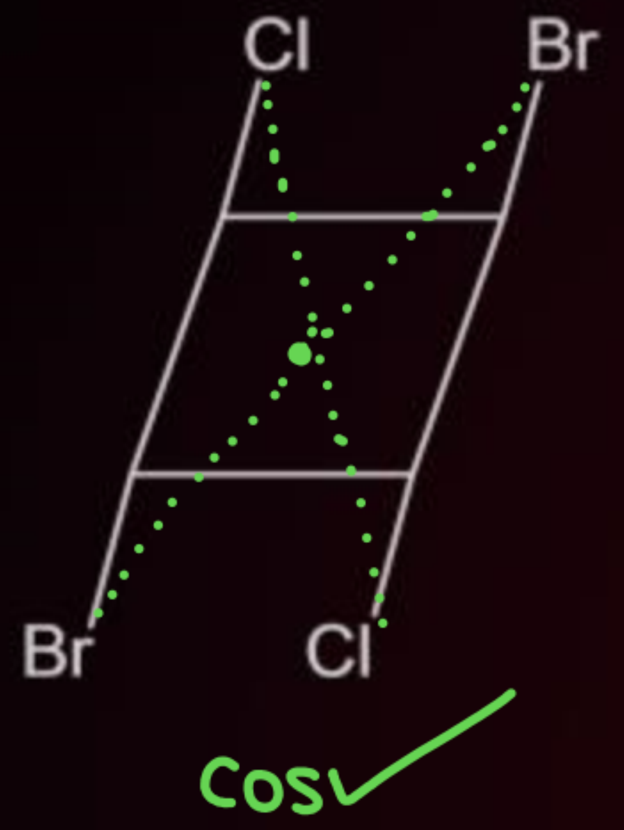
Cos ✓

(8)

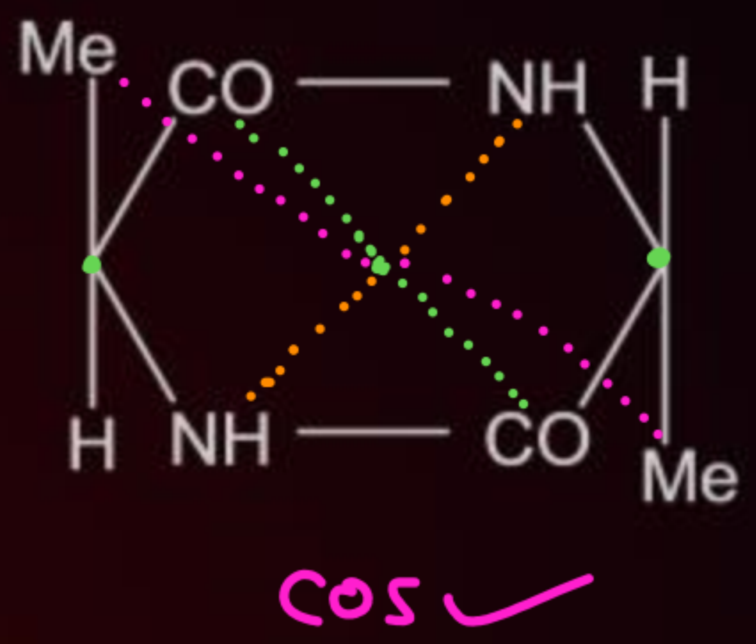


Cos ✓

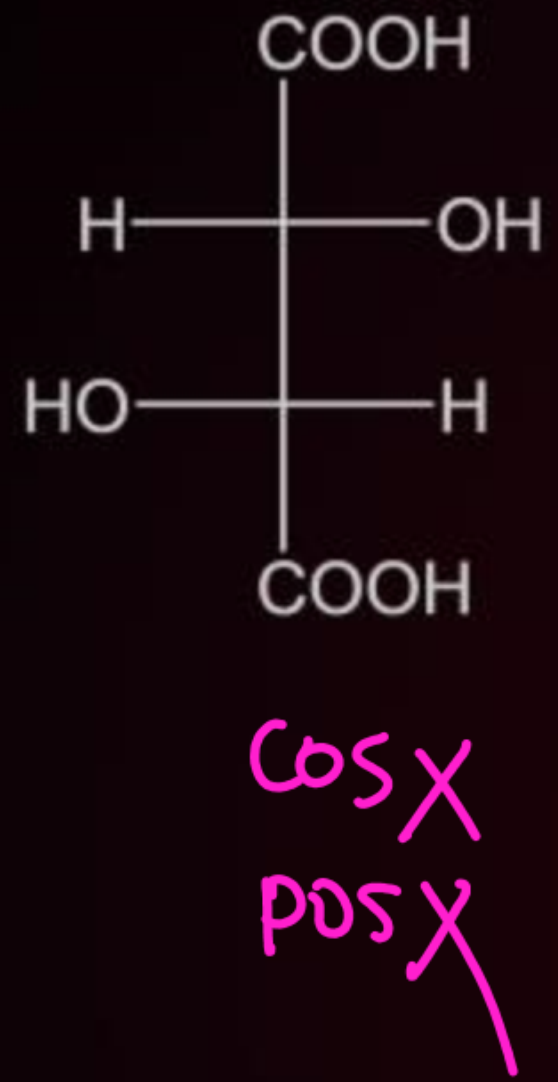
(9)



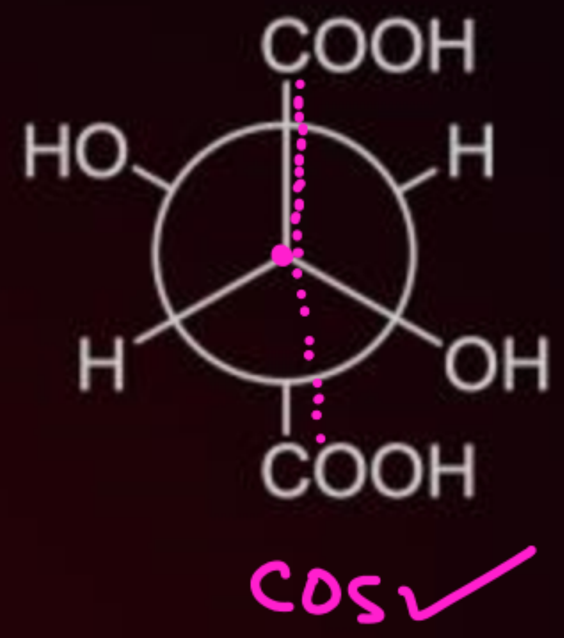
(10)



(11)



(12)



6 timer → 30 min + 20 min extra

THANK YOU
All the Best!!

Condition for a compounds to be optically active

Element of symmetry

(1) Plane of Symmetry (POS)

(2) Center of Symmetry (COS)

Plane of Symmetry (PoS)

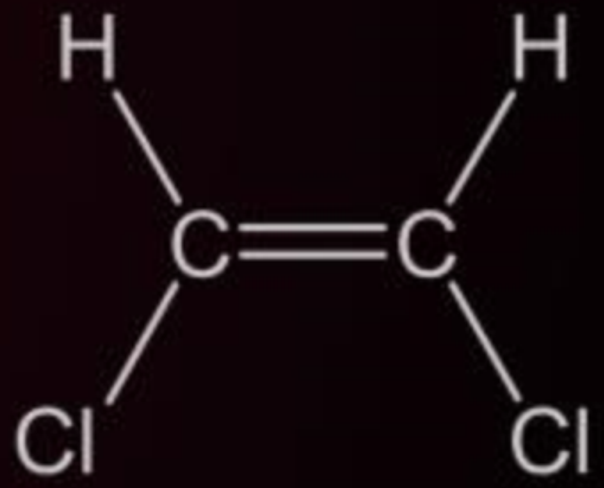
Imaginary plane which divides the molecule in two equal parts and both the parts are mirror image of each other.

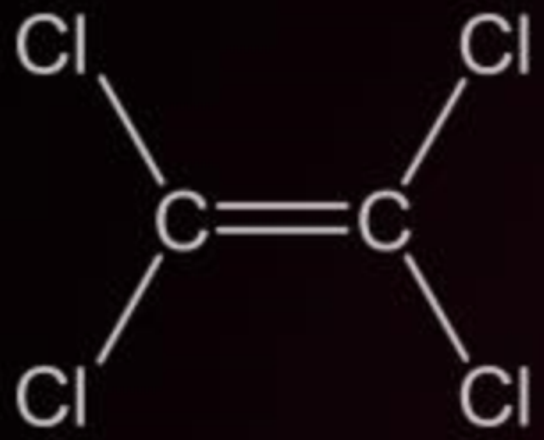
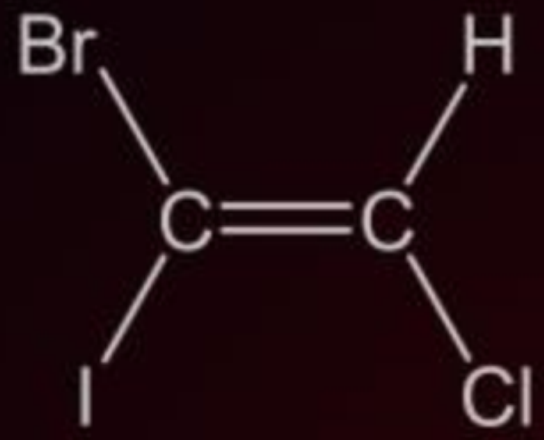
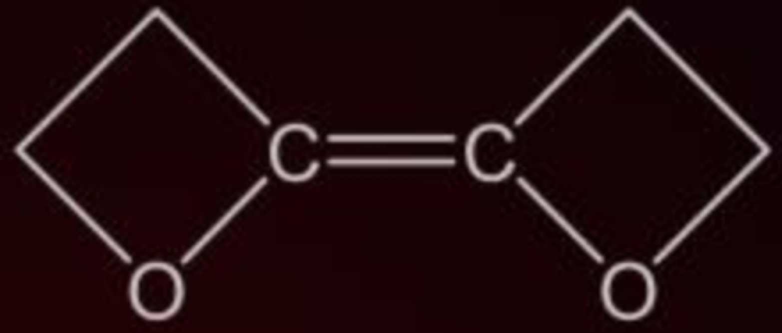
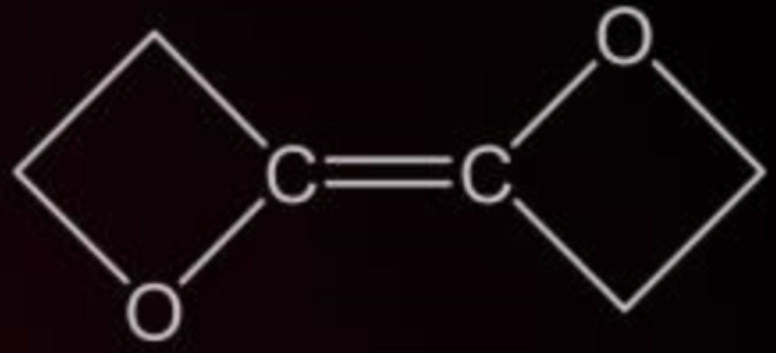
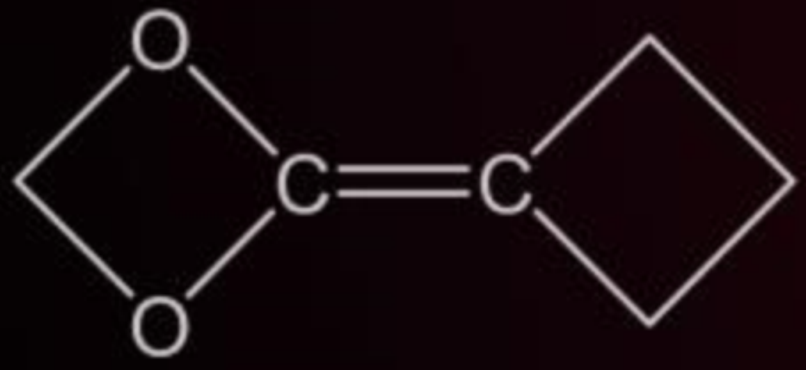
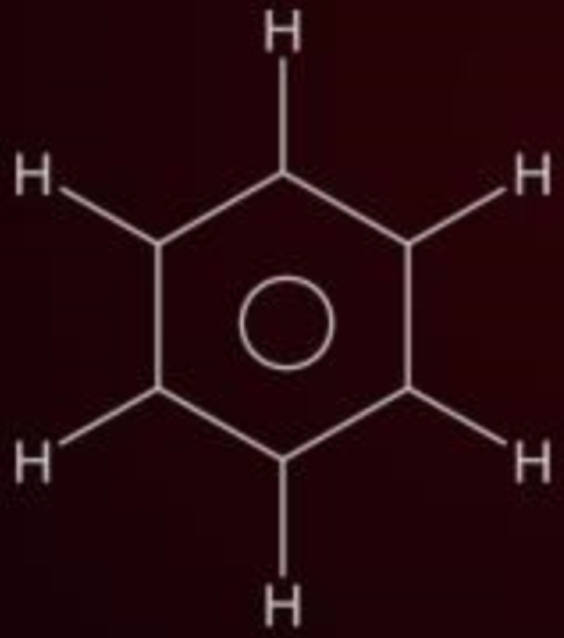
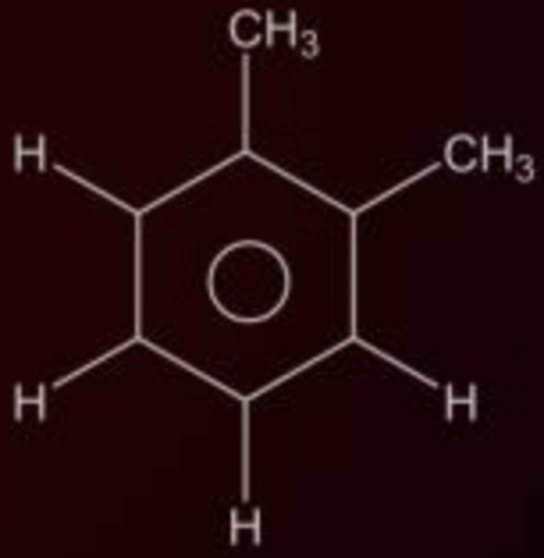
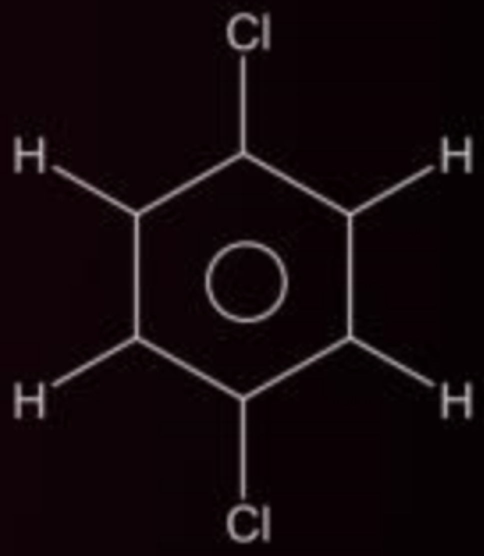
- If PoS is present then compound is optically inactive.

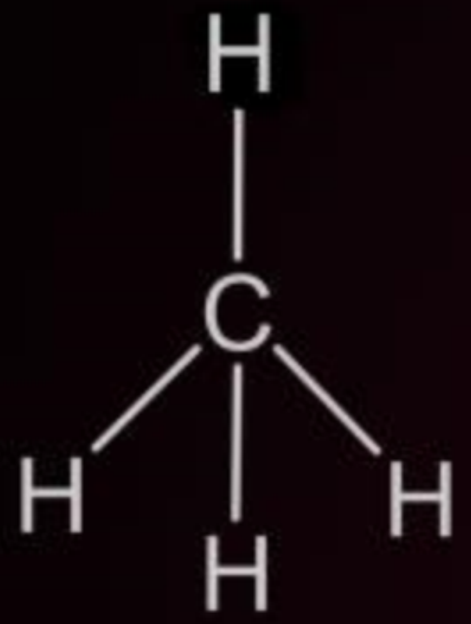
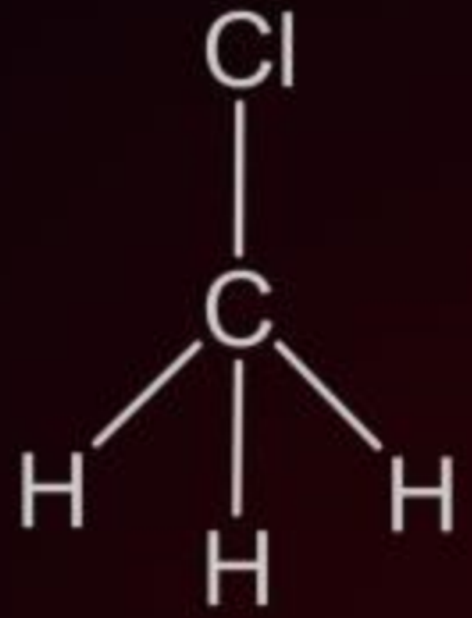
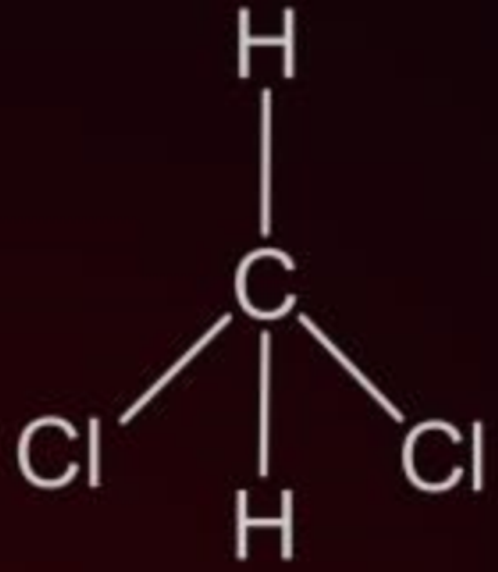
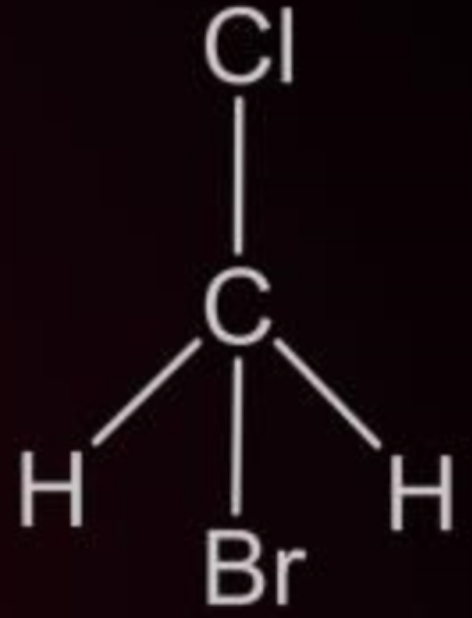
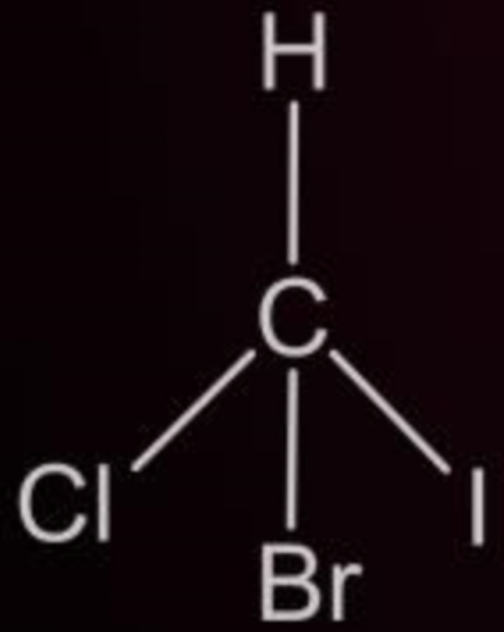




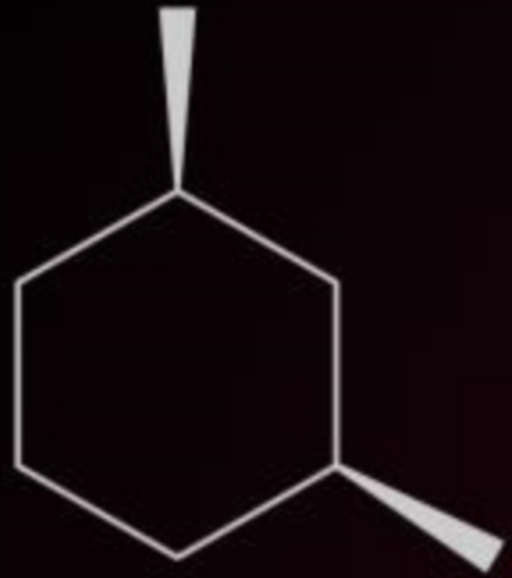


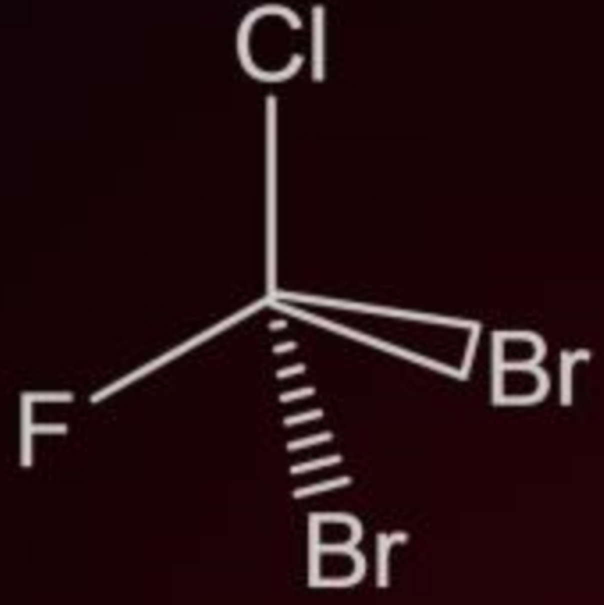


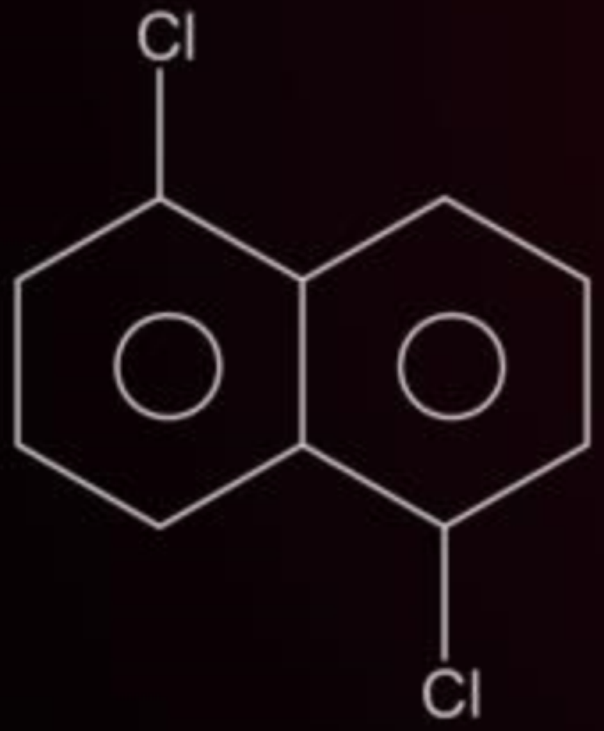


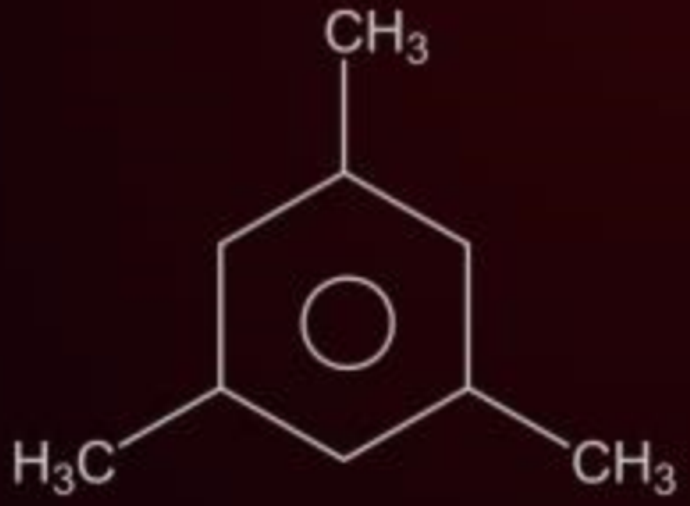



Cl
F
Br
Br


D
H
T
F

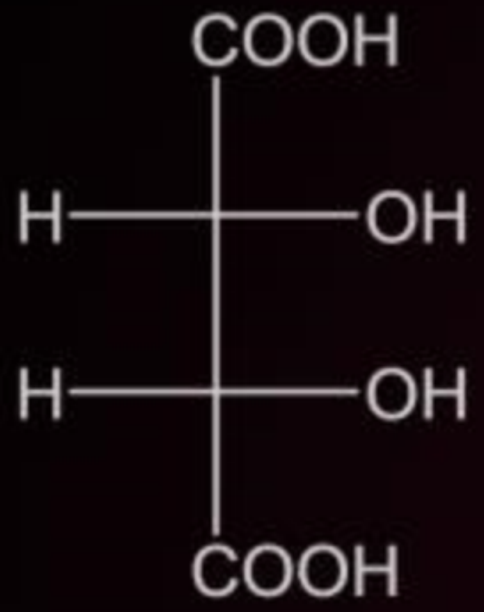

H
H
Cl
H
Cl
Br

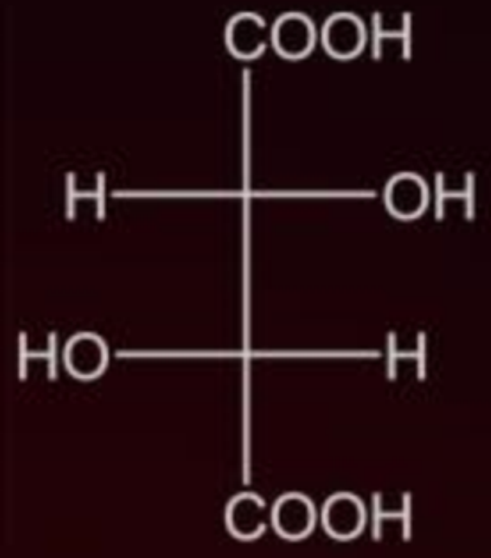

Cl
Cl

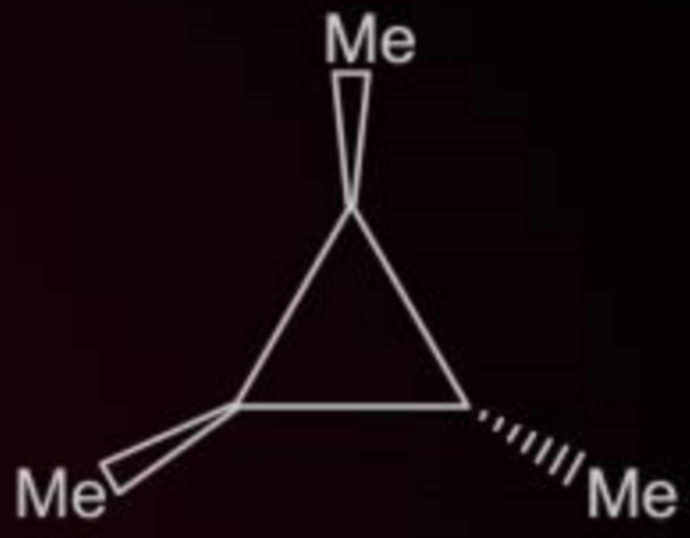

CH3
H3C
CH3




OH
H
D
H
Cl
H
D
OH


COOH
H
OH
H
OH
COOH


COOH
H
OH
HO
H
COOH

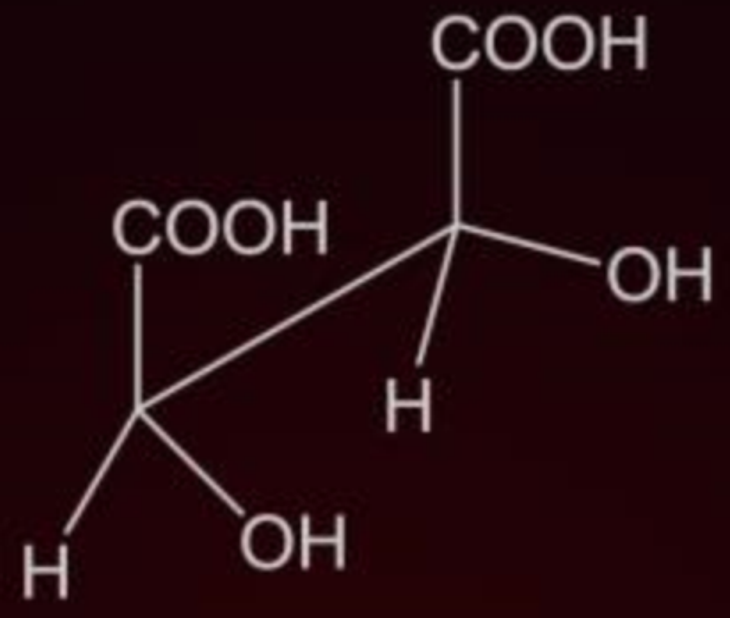

Me
Me
Me

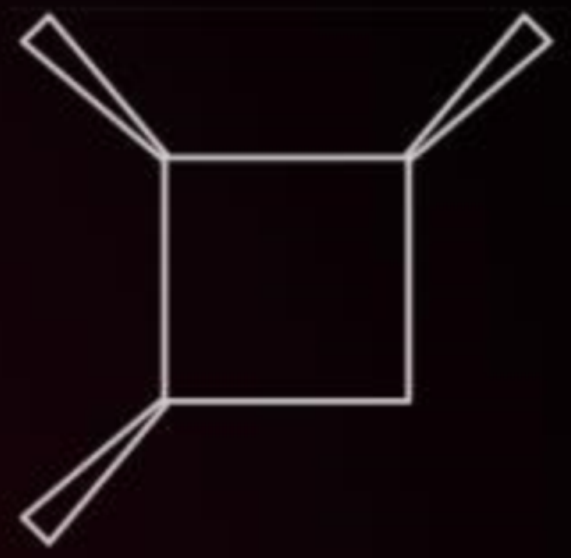

Br




Br
Br




COOH
COOH
OH
H
H
OH



Center of Symmetry (CoS)

Imaginary point at center of molecule from equal atom/group is present at equal distance in opposite direction.

Note:

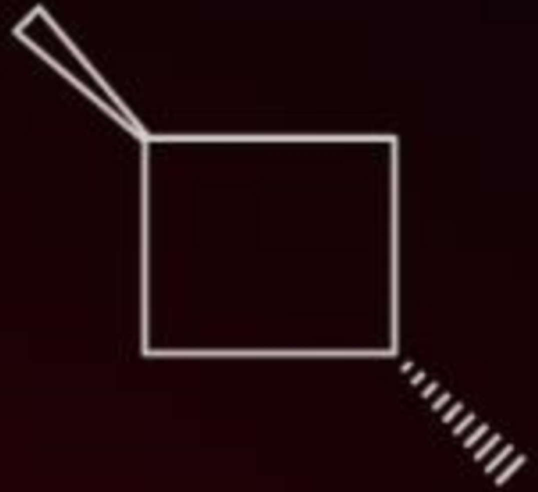
(1) CoS is never present in odd member ring.

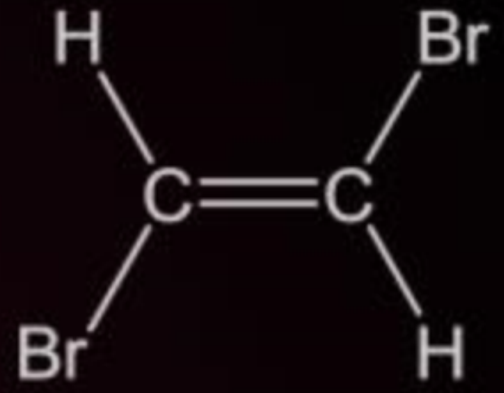
 ,  ,  , etc.

(2) CoS is never present in fisher projection.

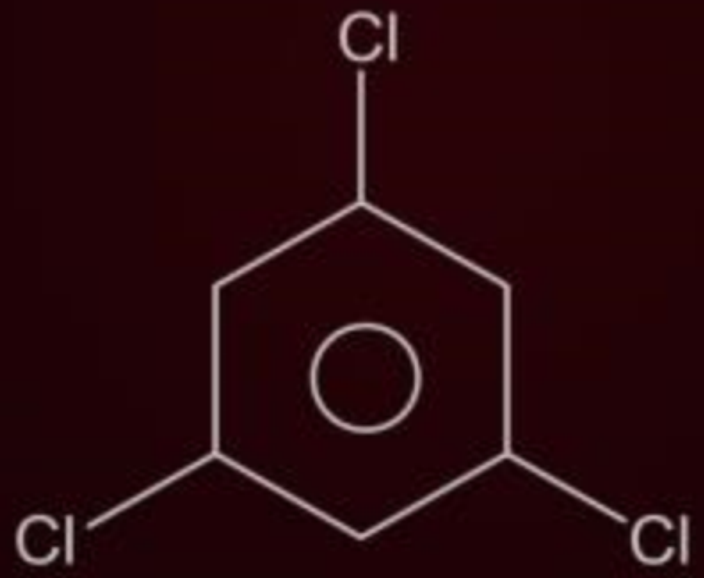


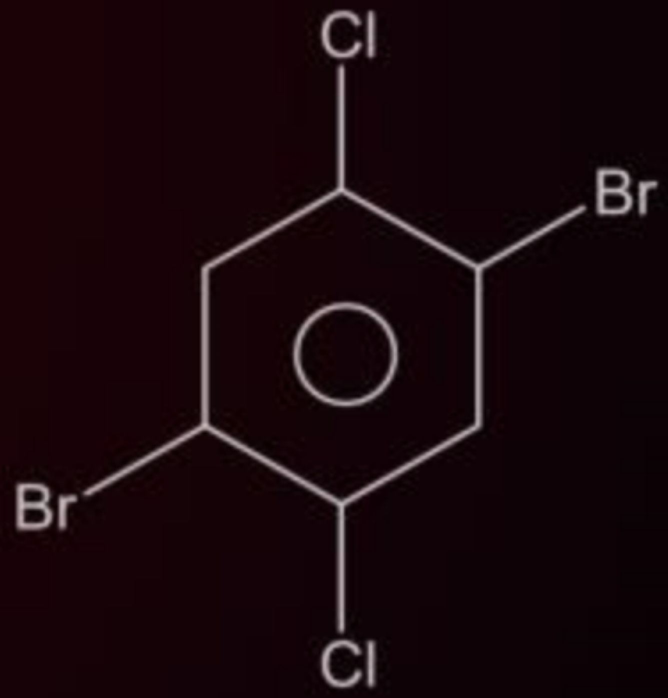





H
Br
C
C
Br
H


Cl
Cl


Cl
Cl
Cl


Cl
Br
Br
Cl

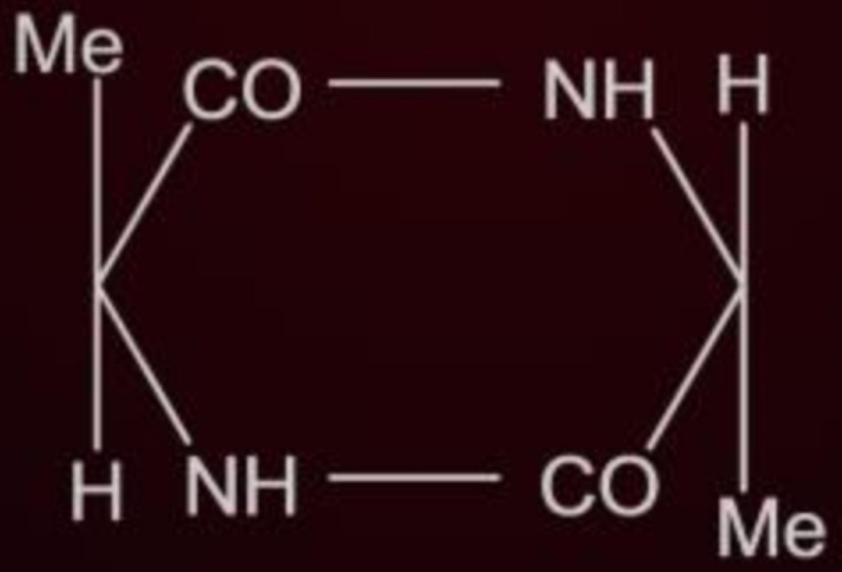


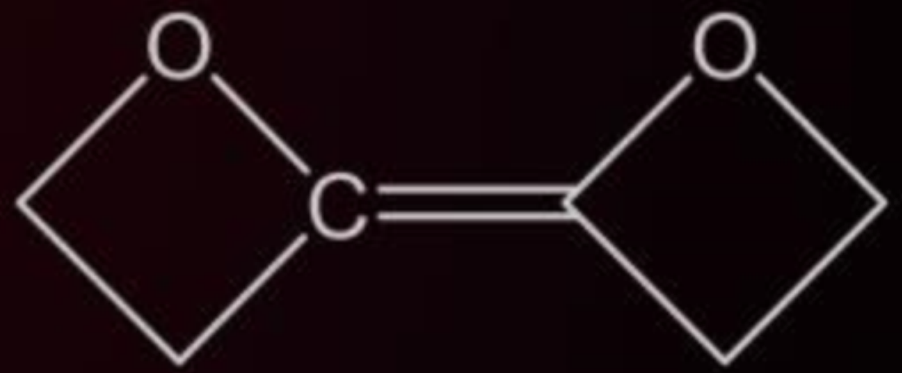



Me
Me


Me
O
O
Me

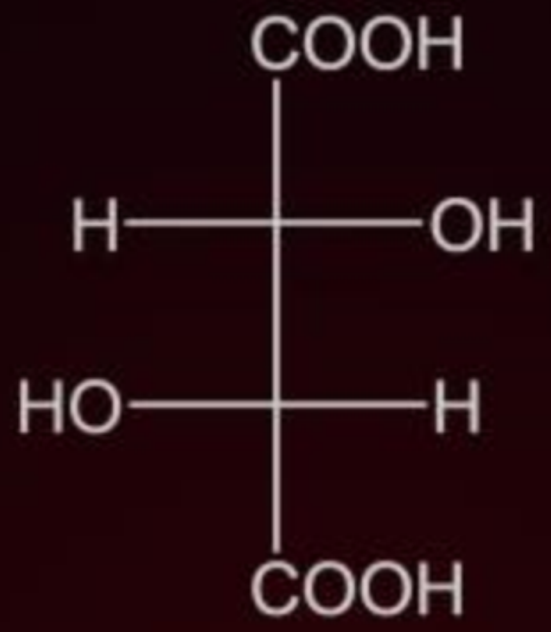

Cl
Br
Br
Cl


Me
CO
NH
H
H
NH
CO
Me

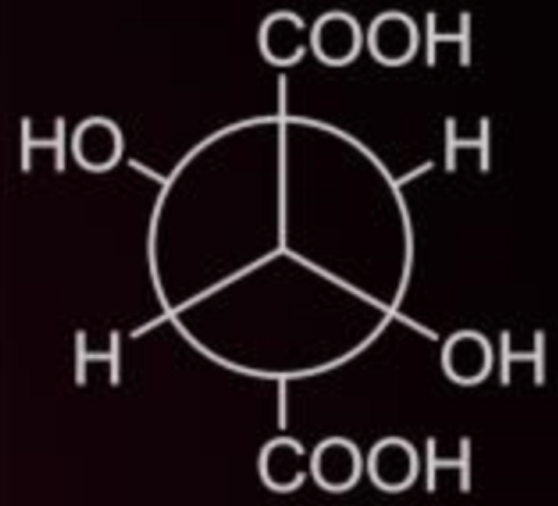

O
C
O



Cl
Br
Br
Cl



COOH
H
OH
HO
H
COOH



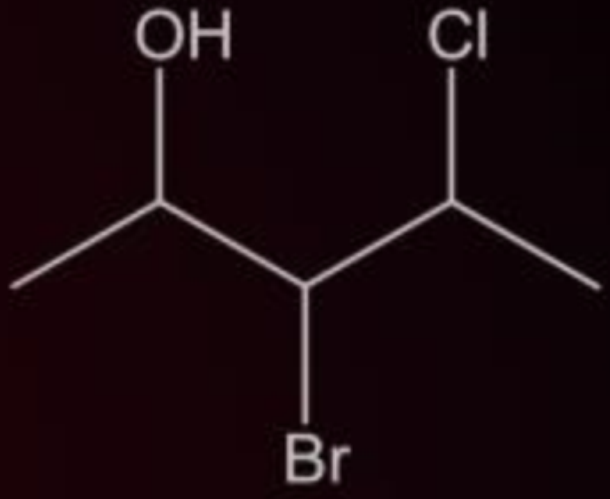
COOH
HO
H
H
OH
COOH

Chiral Center

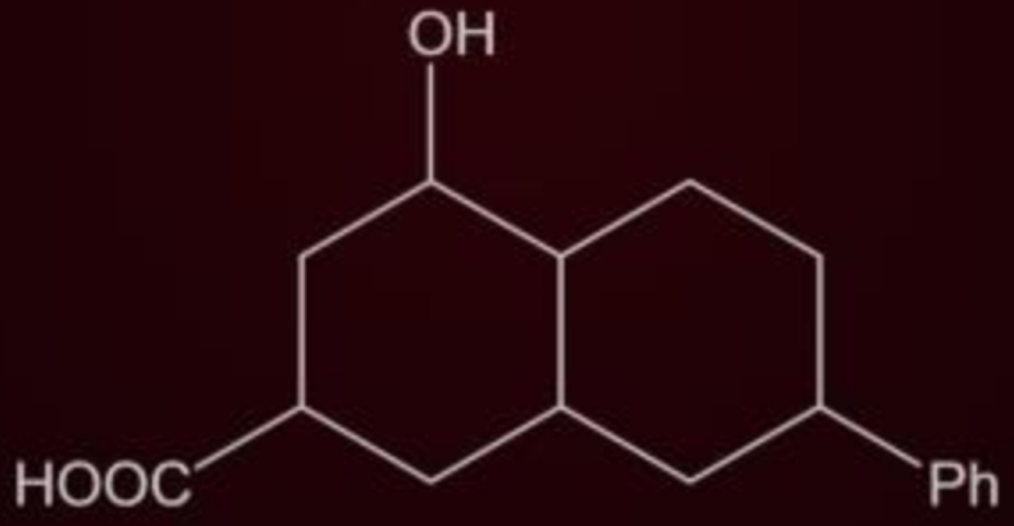
Q. Find number of chiral centers:

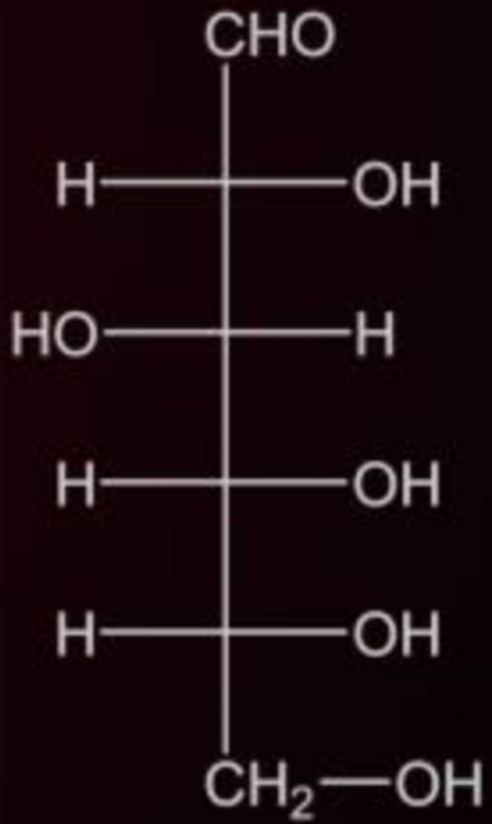


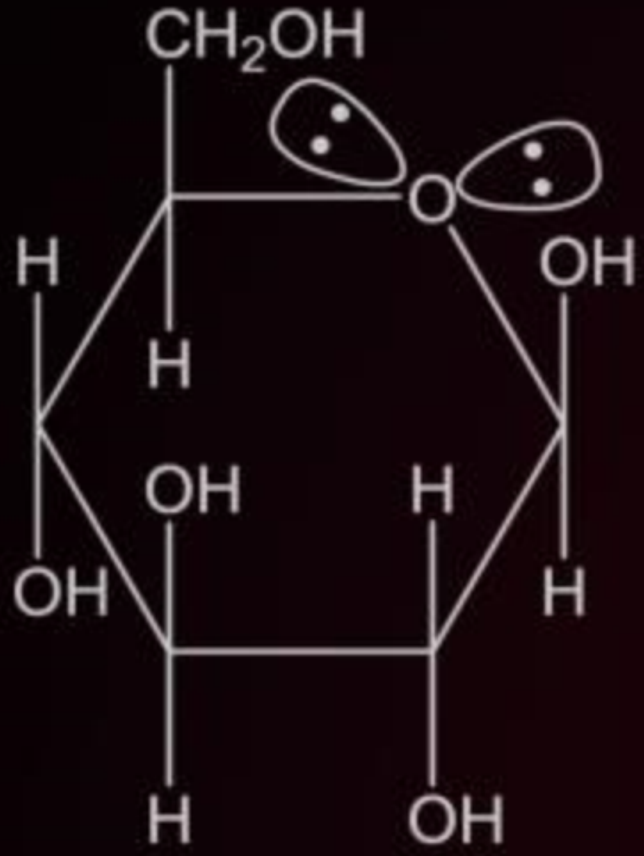




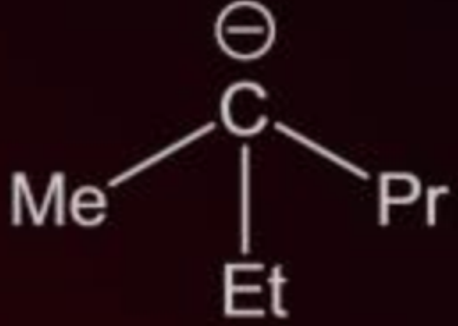


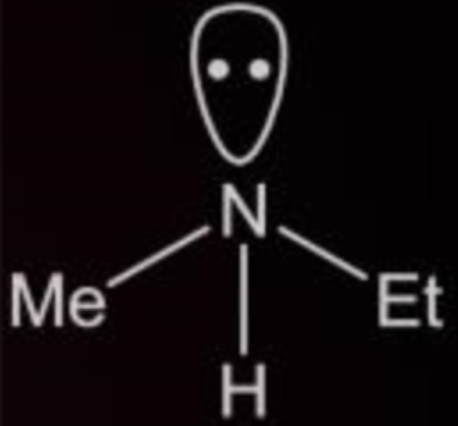


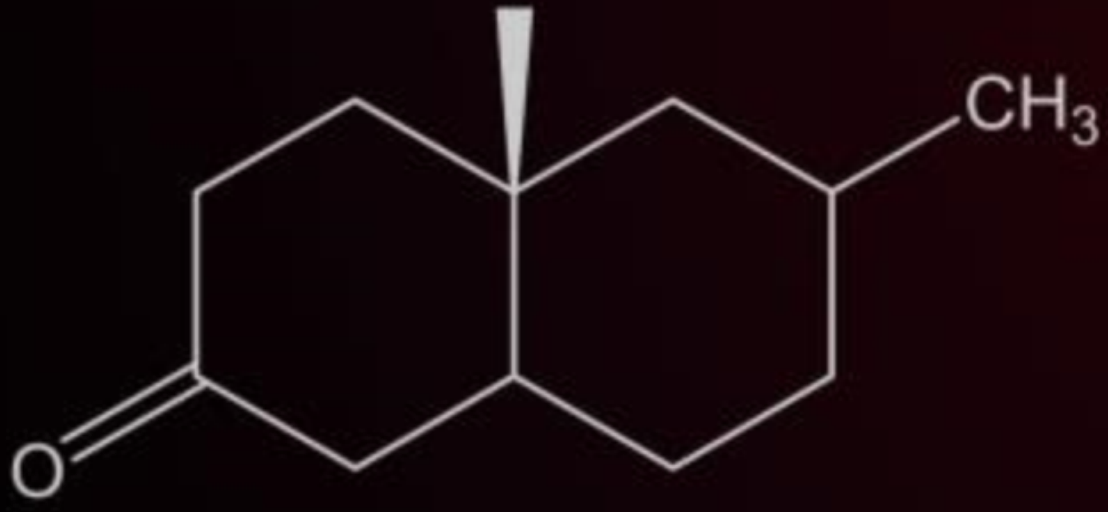


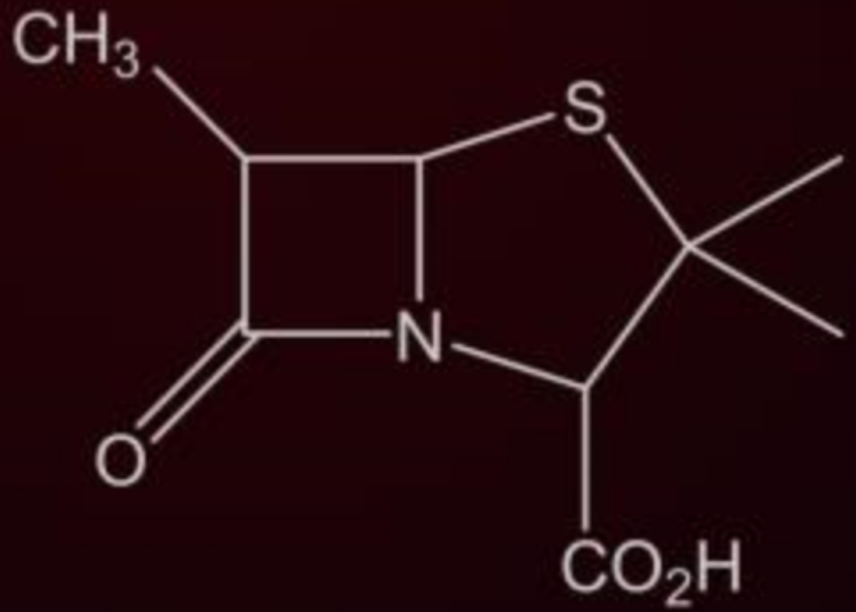

CH2OH
O
H
OH
H
H
OH
H
OH
H
OH
H
OH

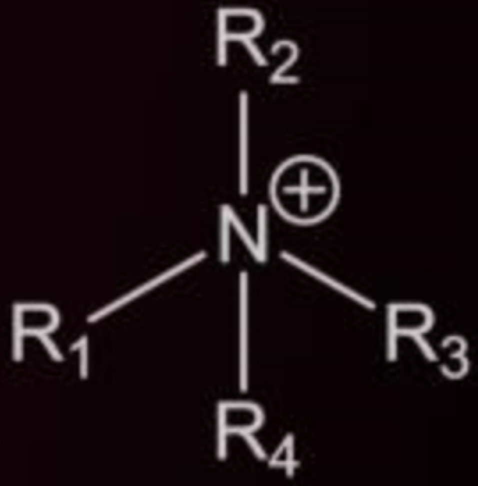

H
O

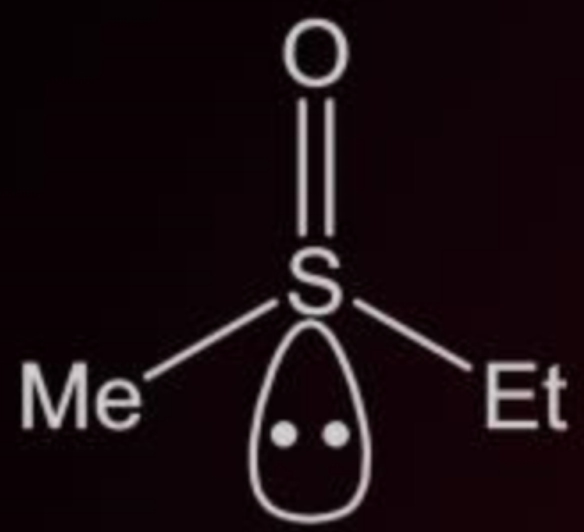

C
Me
Pr
Et


N
Me
Et
H


CH3
O


CH3
S
N
O
CO2H

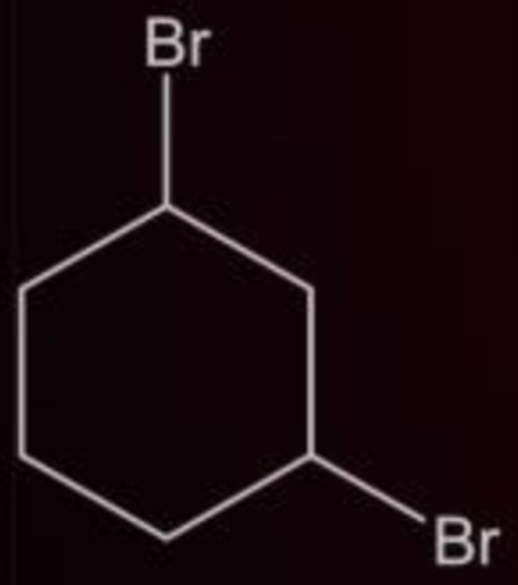

R2
N
R1
R3
R4

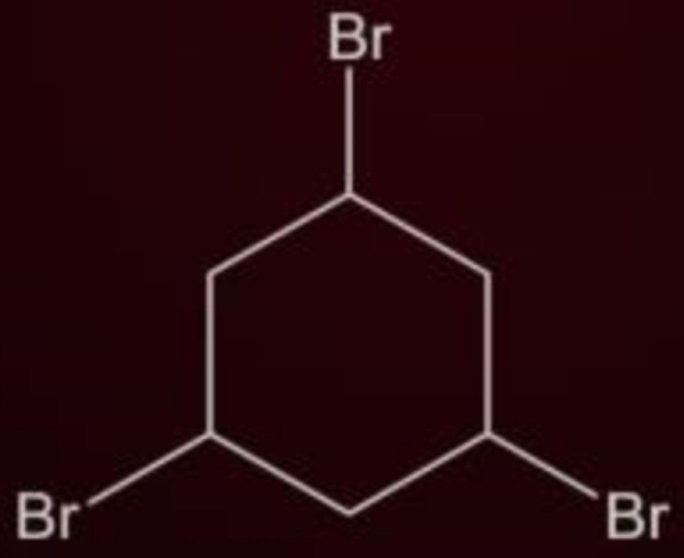

O
S
Me
Et

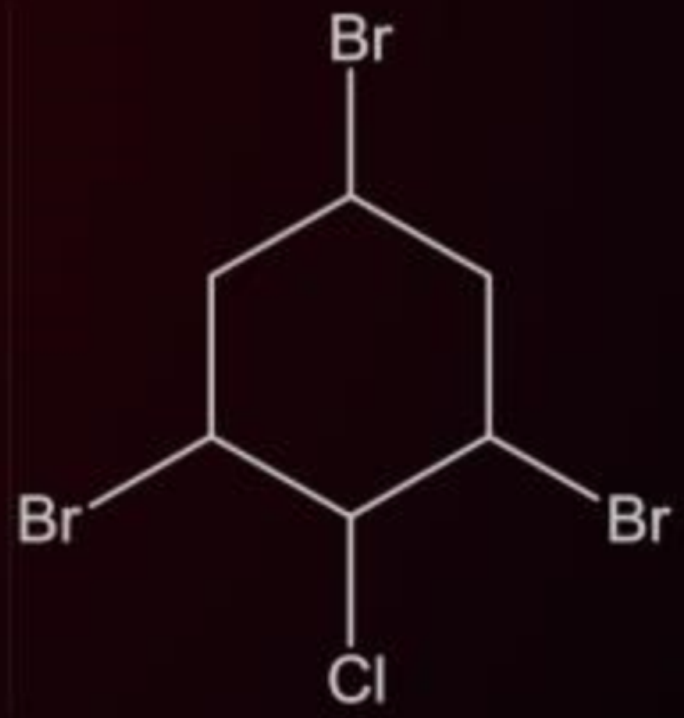

Me
Me

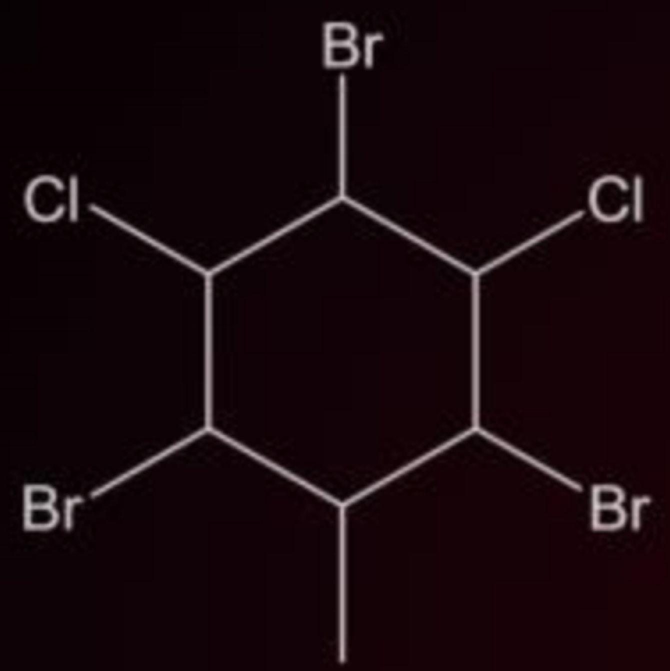
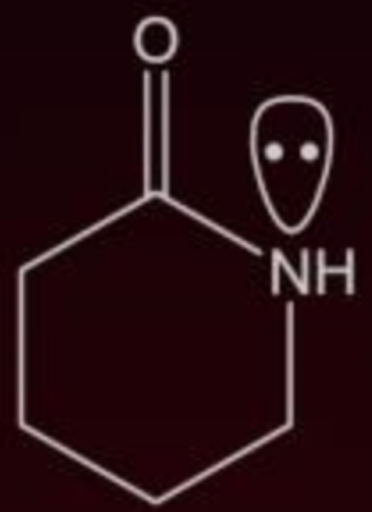
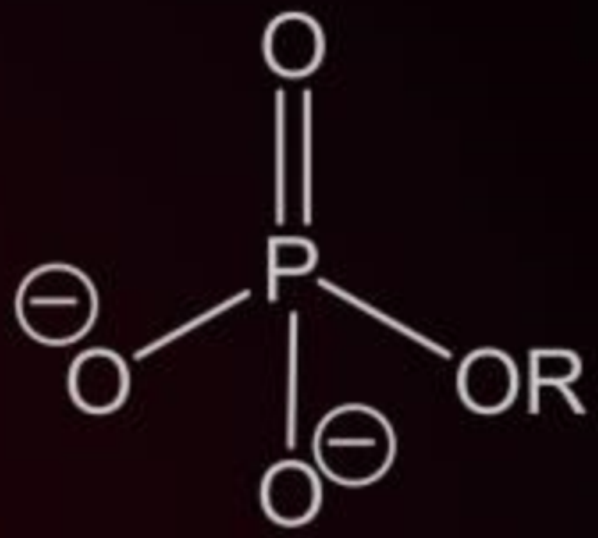

Br
OH


Br
Br


Br
Br


Br
Br
Br


Br
Br
Br
Cl


Br
Cl
Cl
Br
Br

O
NH

O
P
O
OR
O

आज का challange

Today'Goal → 12 Hrs

6hr → Coaching

6hr → Question Practice

2hr ✓

2hr

2hr

Que 1hr < 30 – 20 Q, 30 – 20 Q | 30min | 1.45 | 2hr

1hr < 30 – 20 Q, 30 – 20 Q | 30min | 1.45 | 2hr

1hr < 30, 30

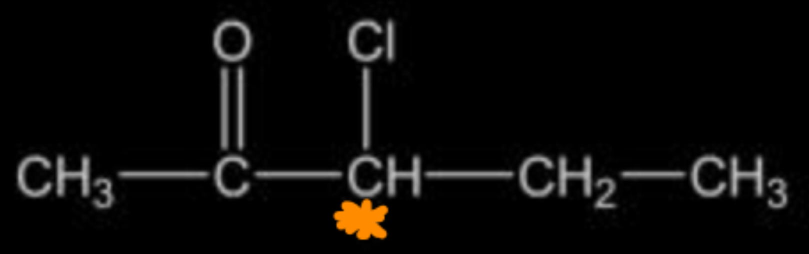
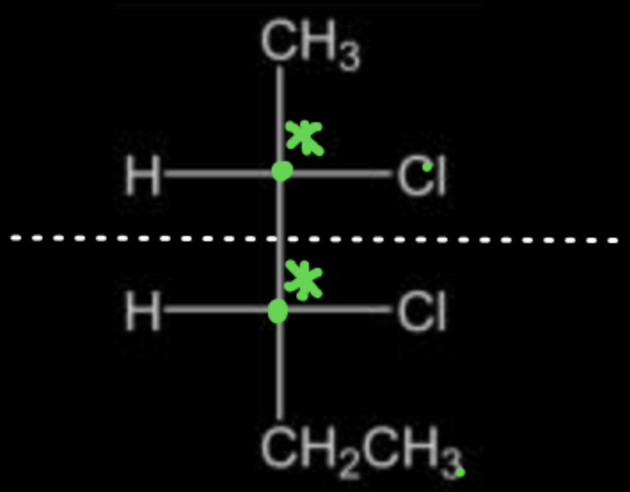
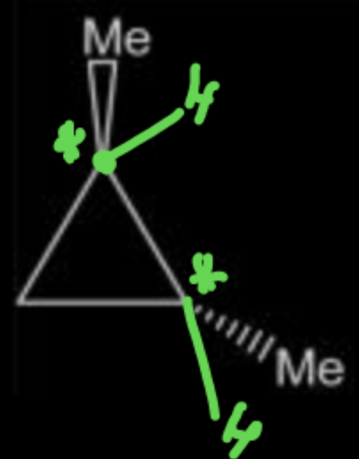
1hr < 30, 30 | 30min | 1.45 | 2hr

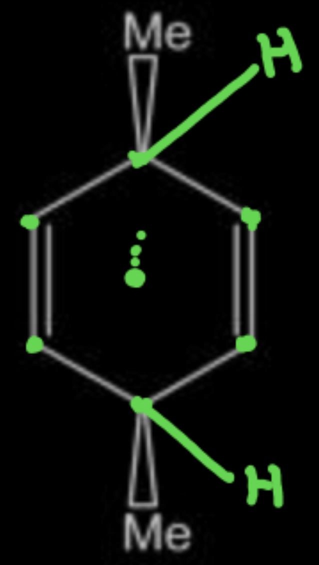
1hr < 30, 30

1hr < 30, 30

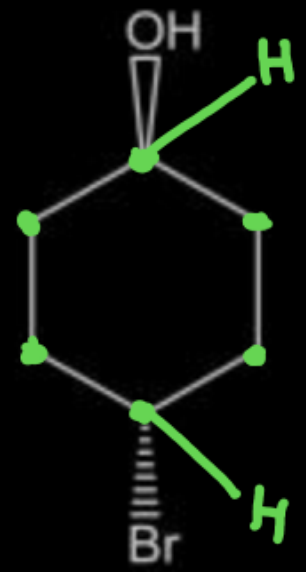
note → There can be no COS in Fischer Projection.

Note: Presence or absence of chiral carbon is not a necessary condition for optical activity.

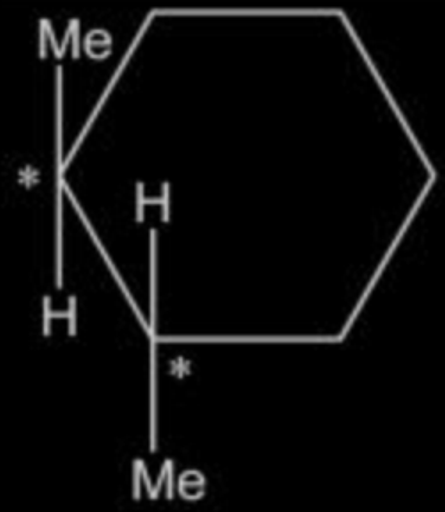
Compound	No. of Chiral Carbon	POS	COS	optical activity
	1	×	×	Unsymmetry ↳ optically active
	2	×	×	Unsymmetrical ↳ optically active
	2	×	×	unsymmetry ↳ optically active



0	✓	✗	Symmetry ↳ optically inactive



0	✓	✗	Symmetry ↳ optically inactive



2	✗	✗	unsymmetry ↳ optically active

non superimposable mirror image.

note → Unsymmetrical Compound → Both POS & COS is absent. → optically active

Symmetrical Compound → Either POS or COS or both are present. → optically inactive

Superimposable Mirror Image

Configuration of Optical Isomerism

1. Erythro and Threo
2. R and S (absolute configuration)
3. D and L (Relative configuration)
4. d/+ and l/− (Experimentally found in polarimeter experimeter)

d/+ → Clockwise

l/− → anticlockwise

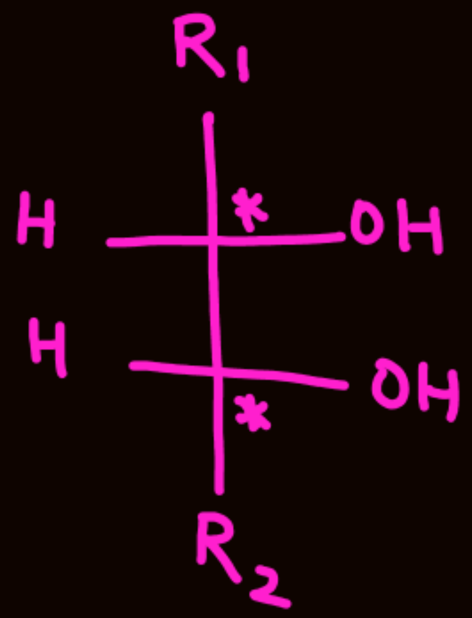
Erythro and Threo Configuration → Fischer Projection

① Min 2 chiral carbon.

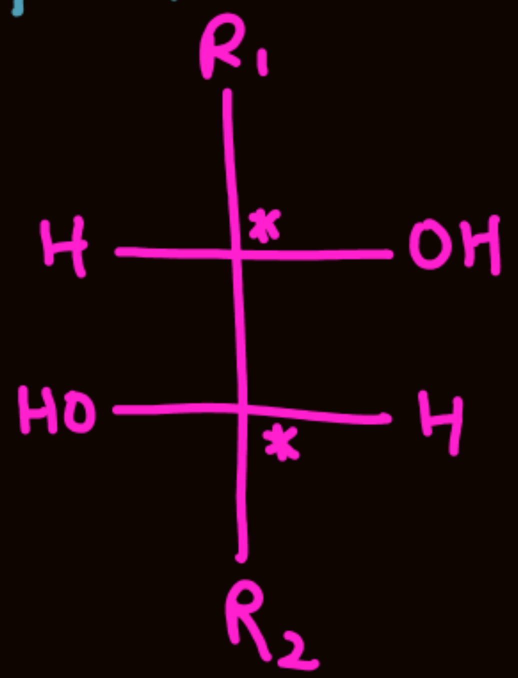
② Samegroup same side → Erythro

Samegroup opp side → Threo

OT	SE
O → opposite, T → Threo	S → Same, E → Erythro

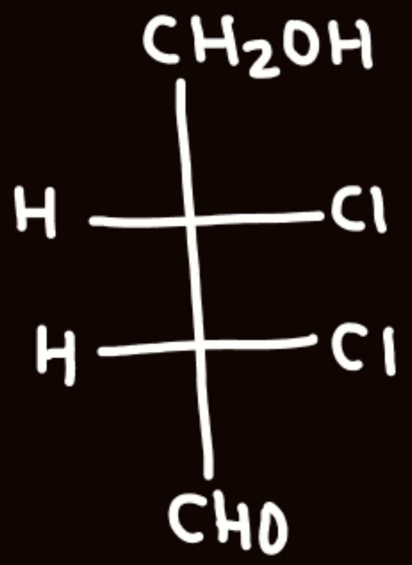


Erythro

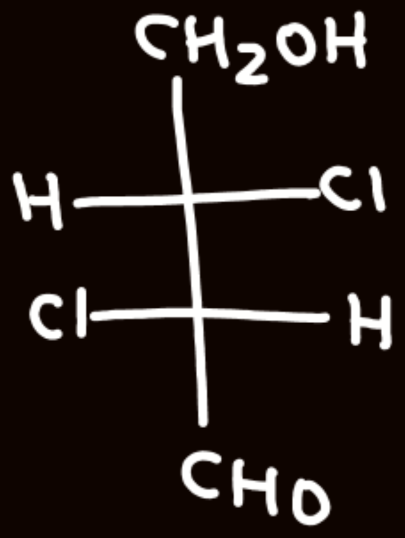


Threo

$R_1 \neq R_2$



Erythro



Threo

R and S Configuration in Fischer Projection

→ It is defined for all chiral carbon.

(R1) → assign Priority to all 4 different atom/group.

If 4th priority is on Vertical line

VAS VCR

1 → 2 → 3

Acw → S
cw → R

If 4th Priority is on horizontal line

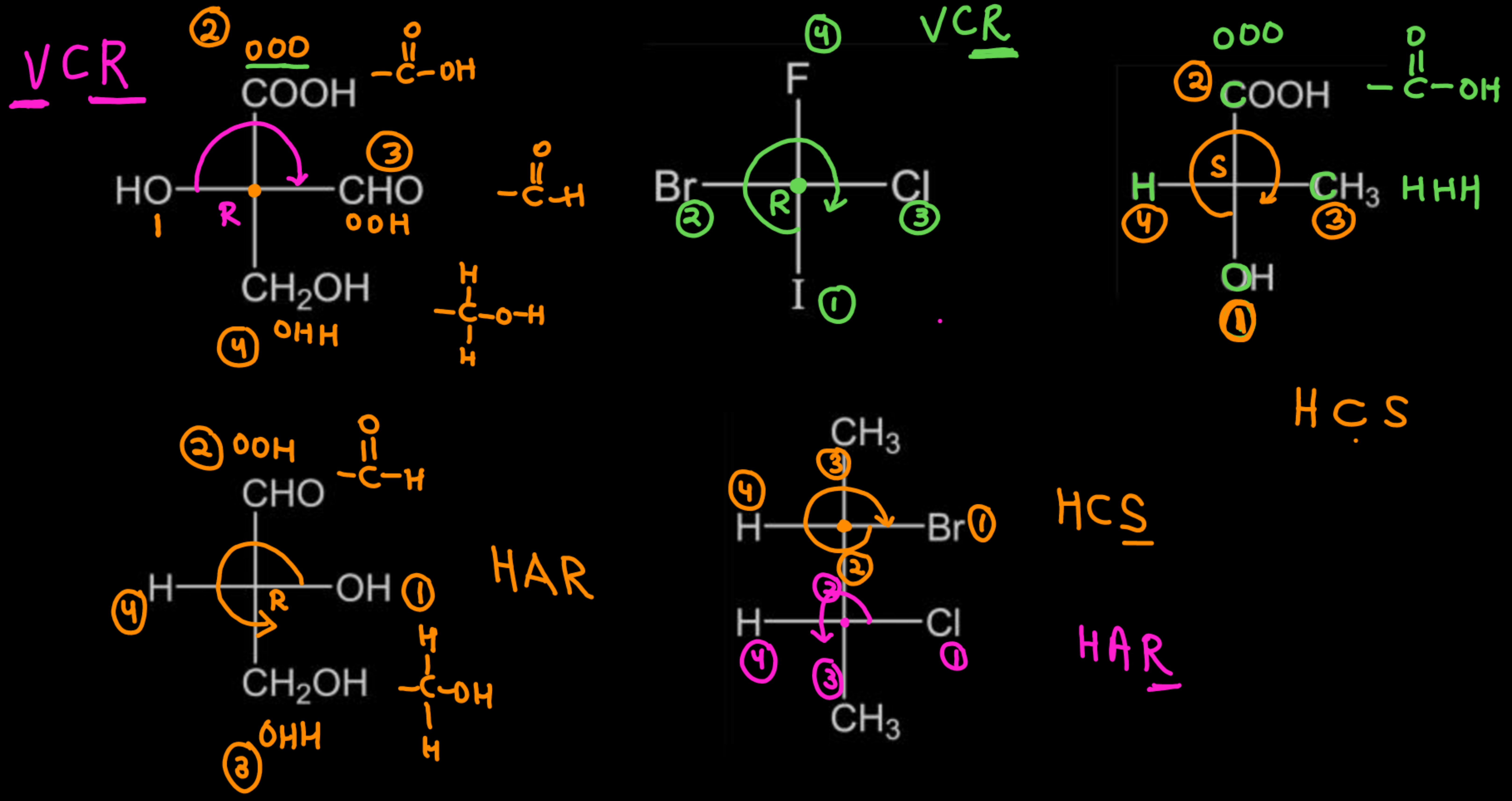
HAR HCS

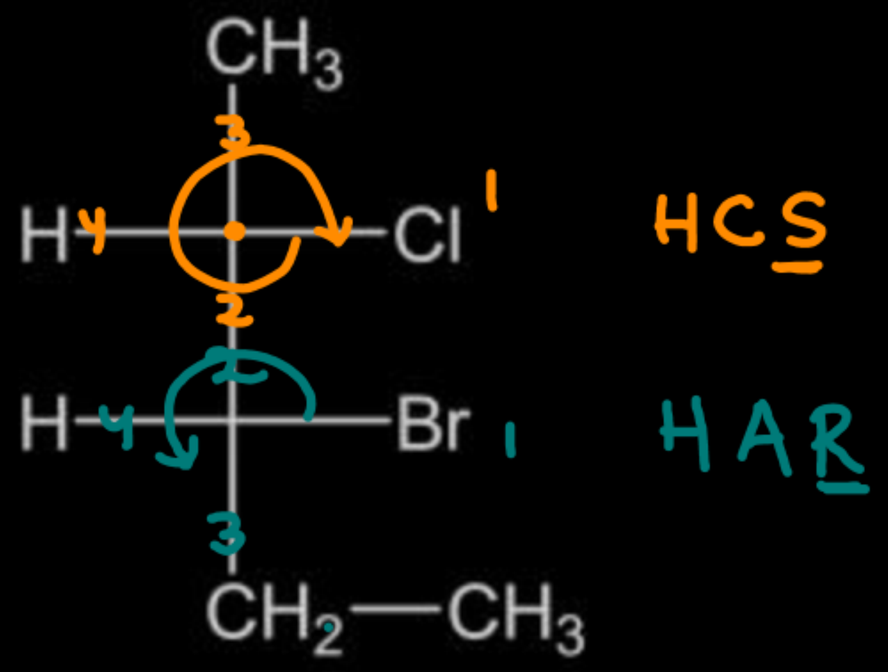
1 → 2 → 3

Acw → R
cw → S

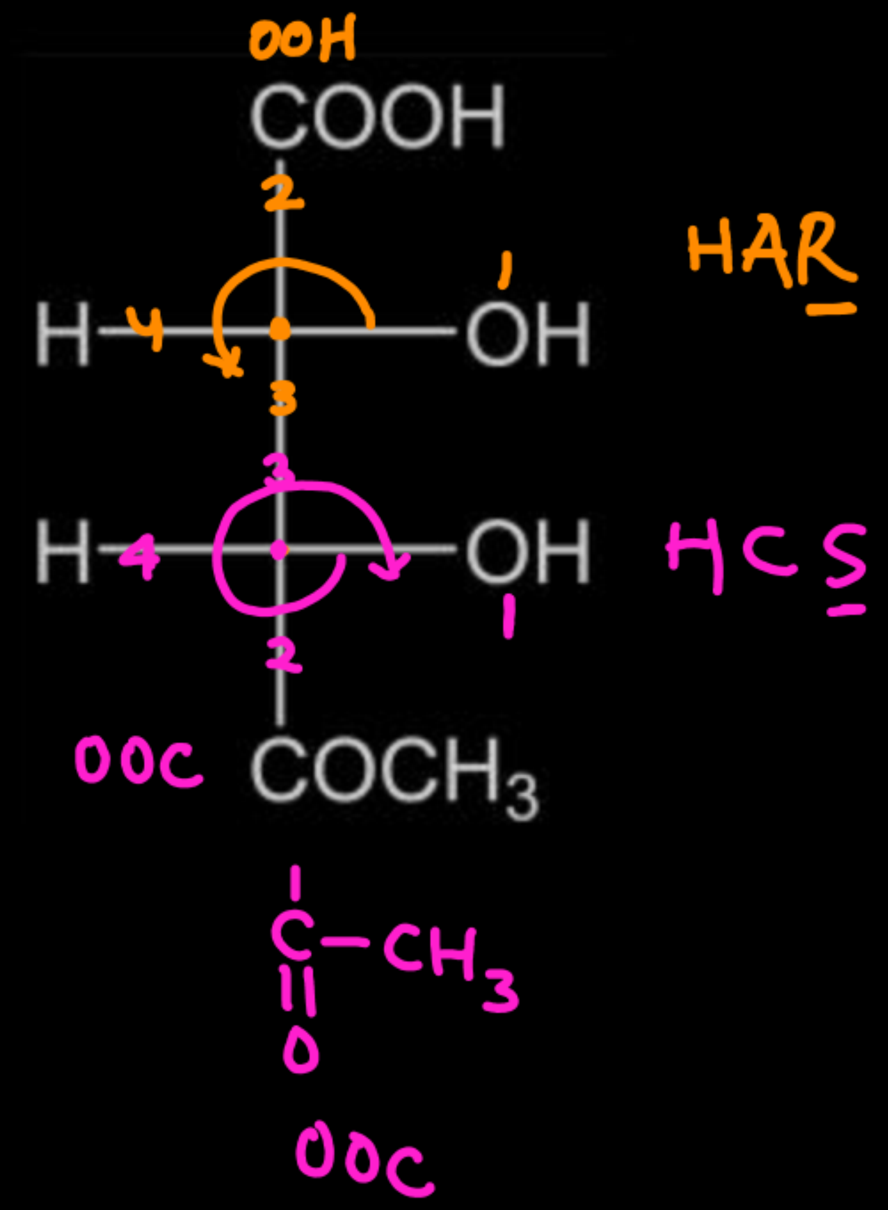
R → Rectus → clockwise

S → Sinister → Anticlockwise

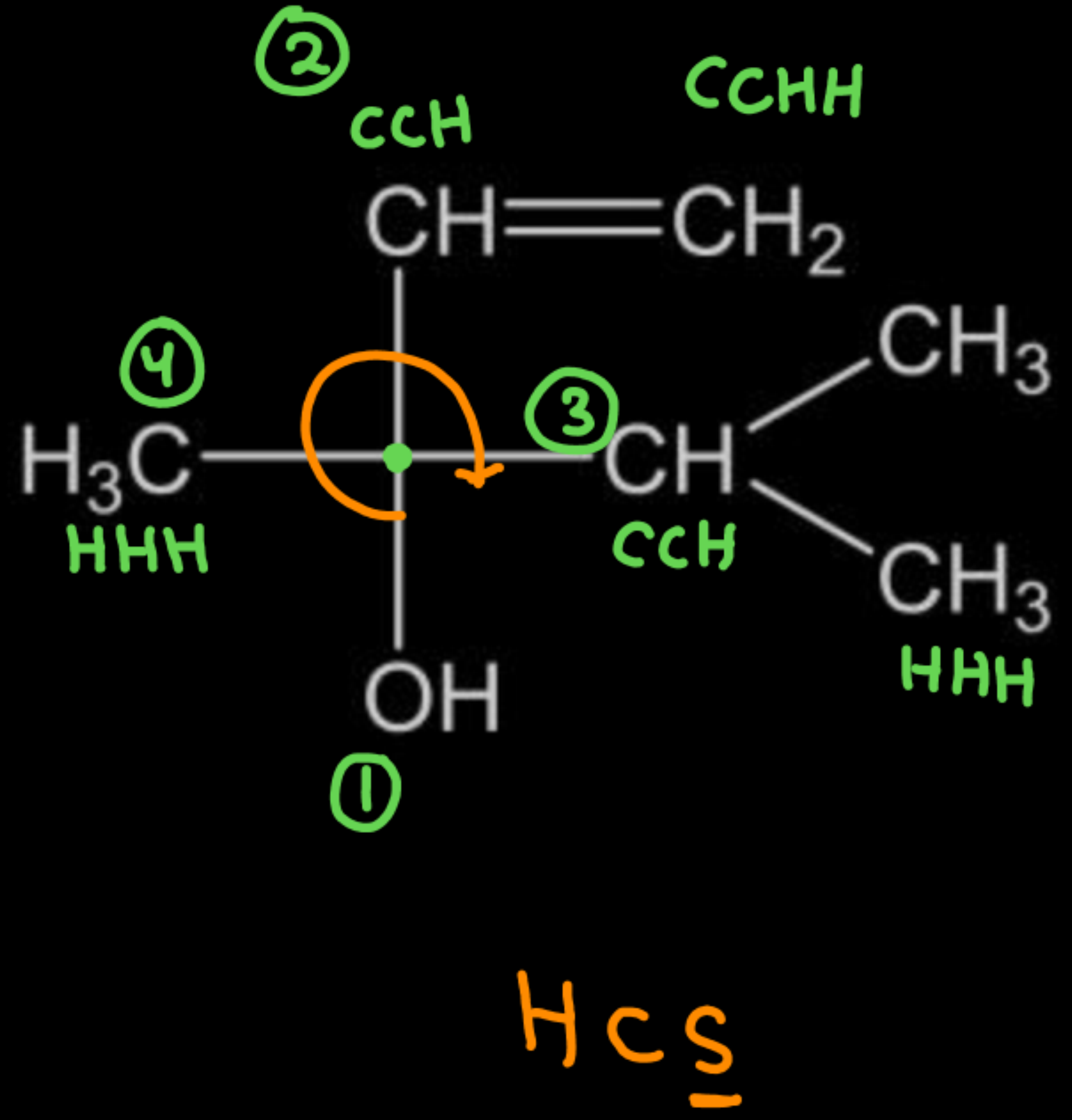

VCR
COOH
HO
CHO
CH2OH
R
F
Br
Cl
I
VCR
COOH
H
CH3
OH
S
HHH
HCS
CHO
H
OH
CH2OH
HAR
CH3
H
Br
H
Cl
CH3
HCS
HAR



CH3
H
Cl
Br
CH2—CH3
HCS
HAR

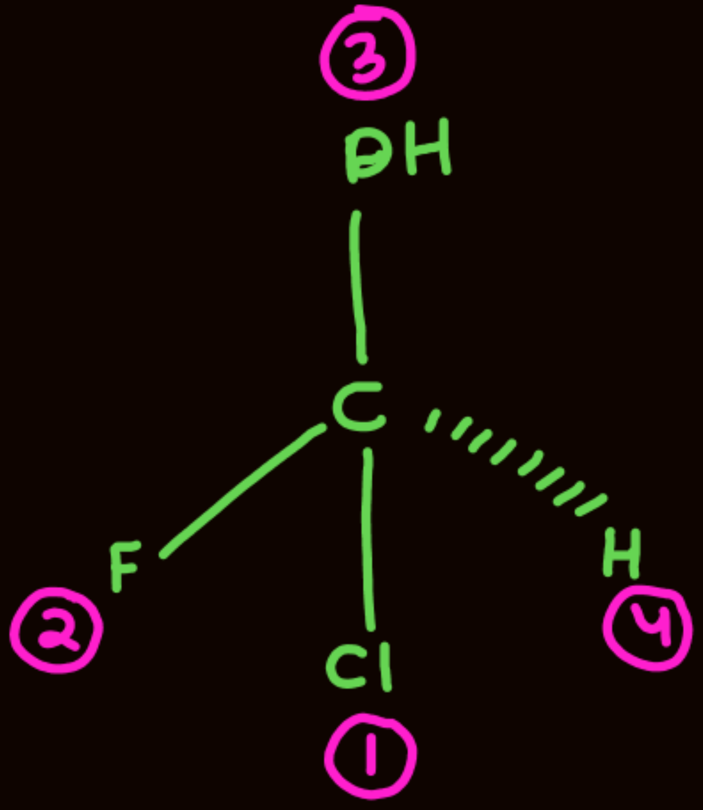


OOH
COOH
H
OH
COCH3
OOC
HAR
HCS
C—CH3
O
OOC



CCH
CCHH
CH═CH2
CH3
H3C
CH
HHH
CCH
OH
HCS

R–S configuration in wedge-dash



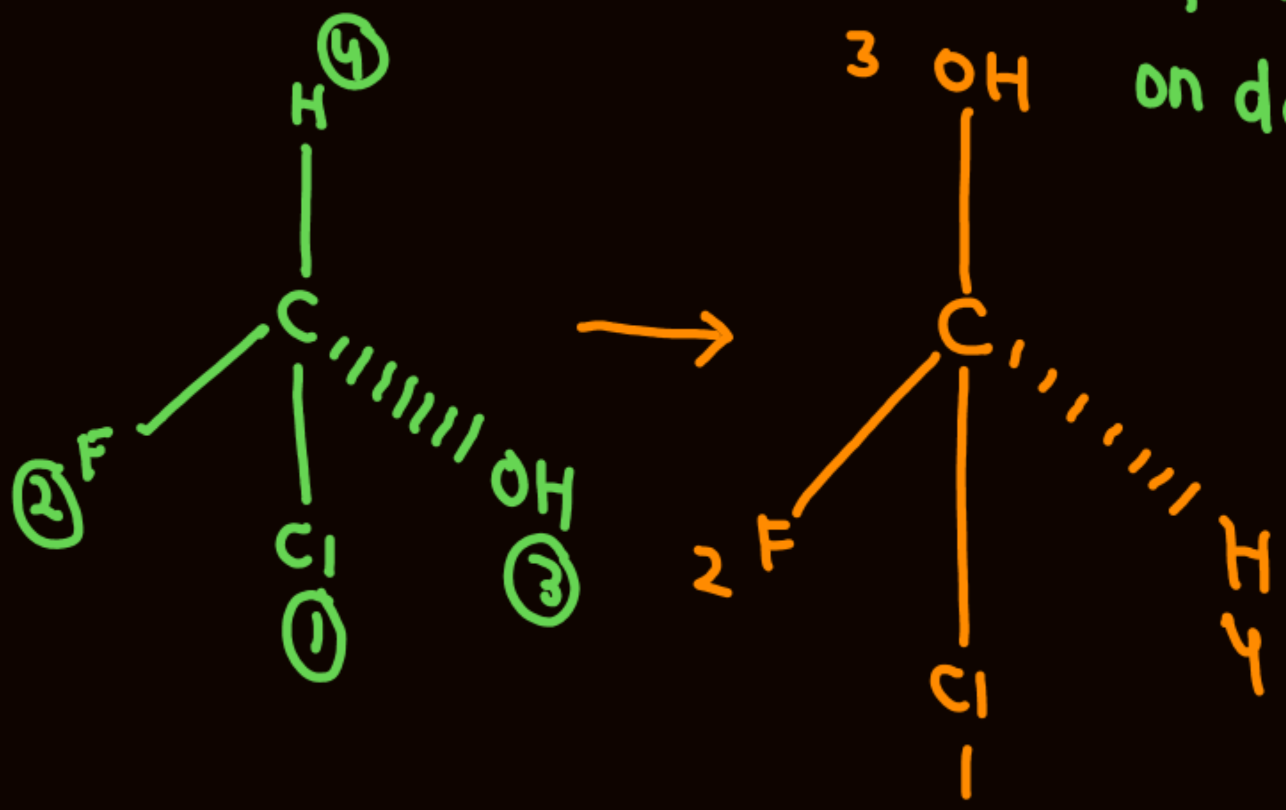
DAS

DCR

If 4^{th} Priority is on dash then $1 \rightarrow 2 \rightarrow 3$

ACW → S

CW → R



If 4^{th} priority is not on dash then bring 4^{th} priority on dash by interchanging.

↓

Reverse the configuration.

~~R~~ → S

~~S~~ → R

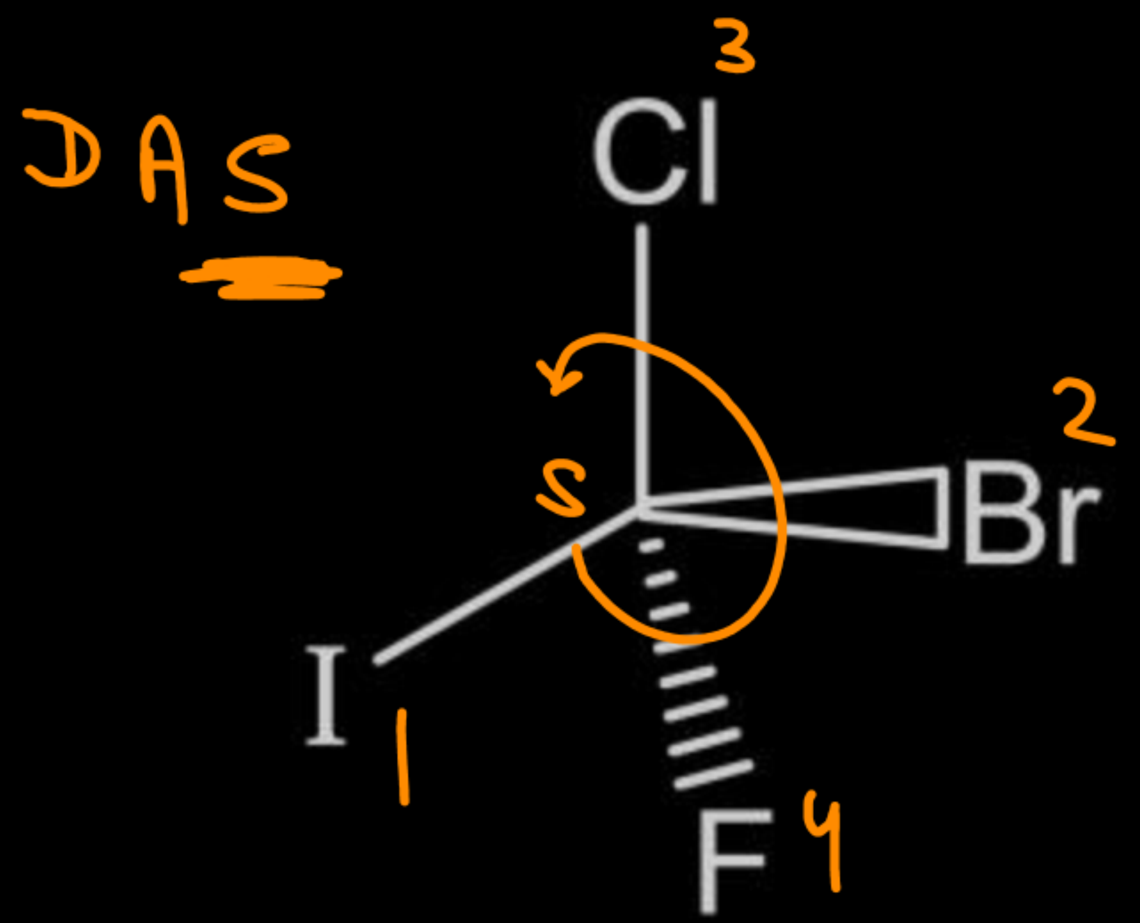
R-S configuration in Wedge-Dash

R 1: If lowest priority on dashline 1 ⟶ 2 ⟶ 3

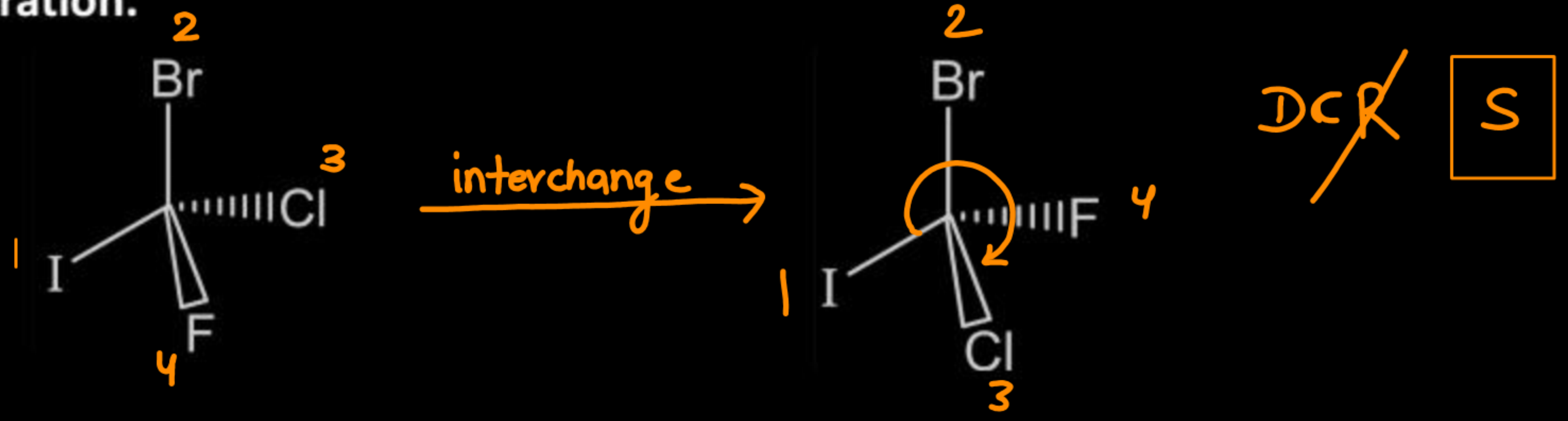
DAS DCR

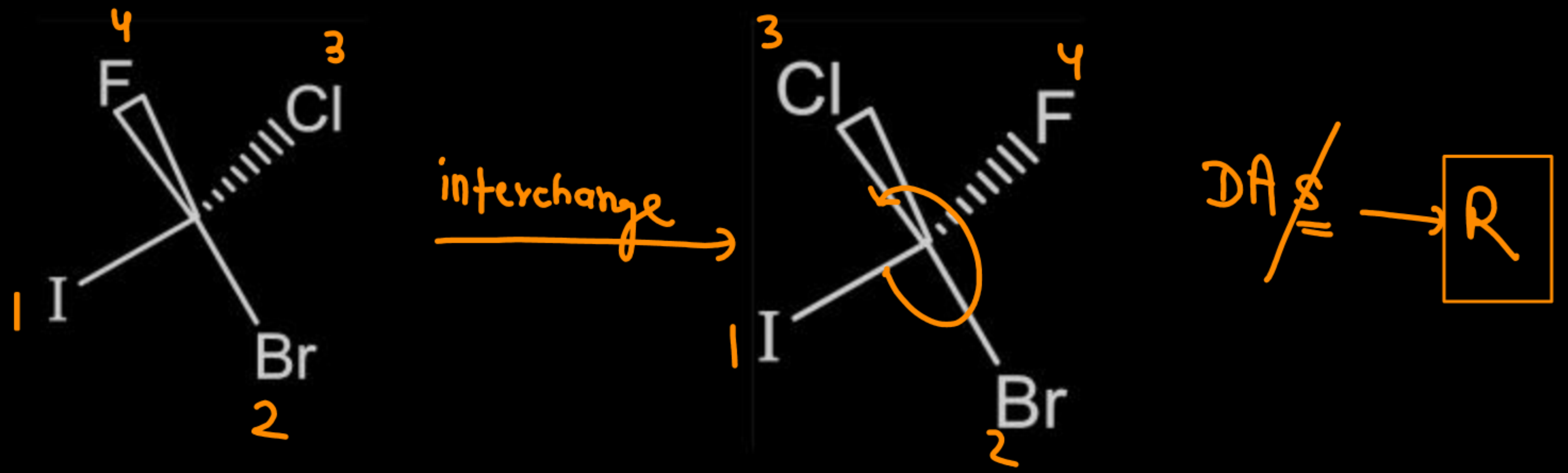
CW ⟶ R

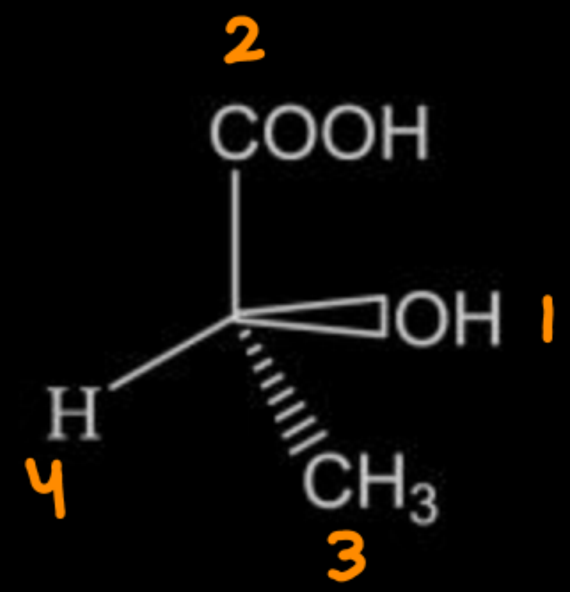
ACW ⟶ S



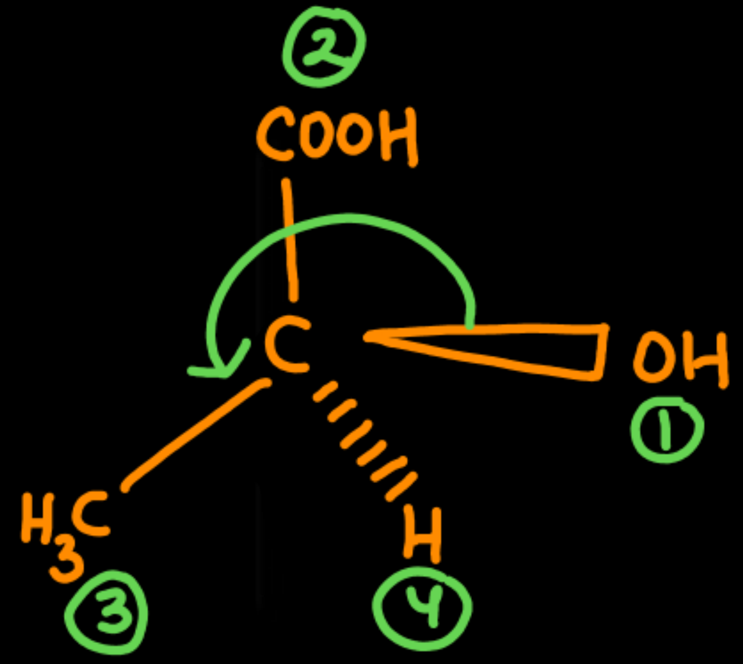
R 2: If lowest priory is not an dashline then it is exchange with dashgroup and reverse the configuration.





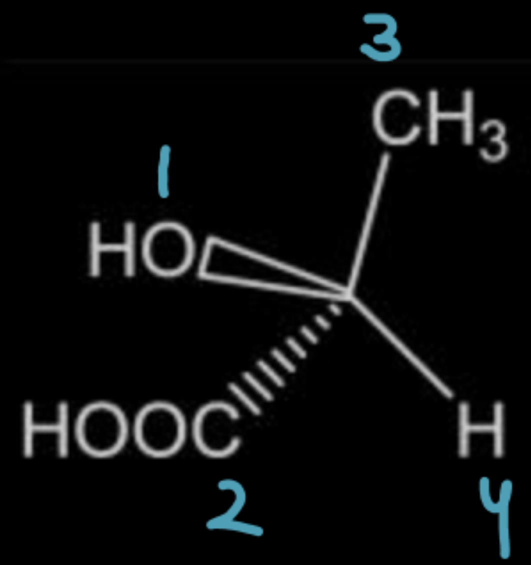


2
COOH
OH 1
H
4
CH3
3

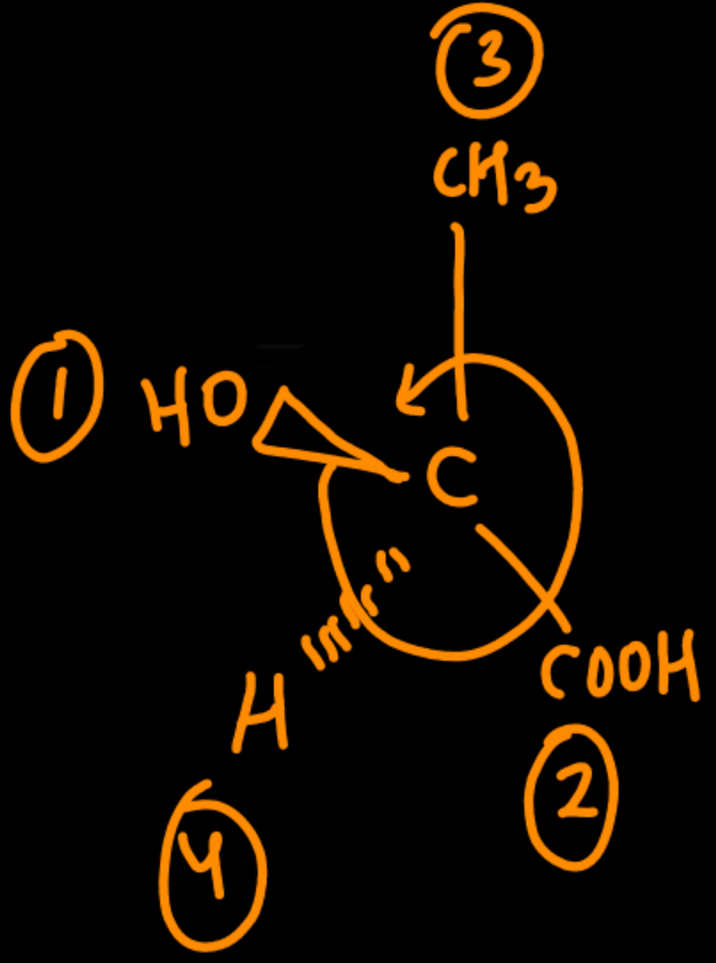


2
COOH
C
OH
1
H3C
3
H
4

DAS → R

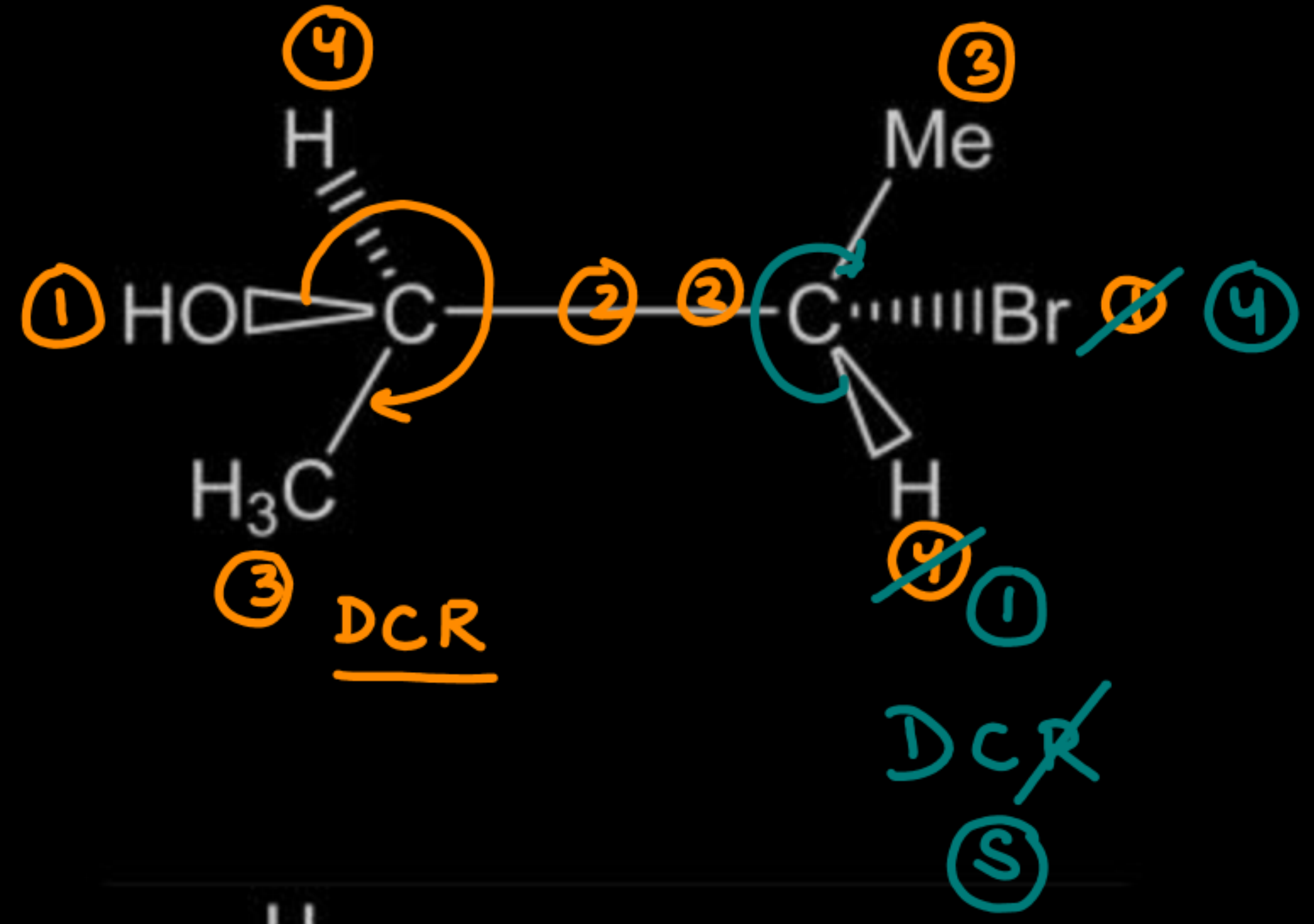


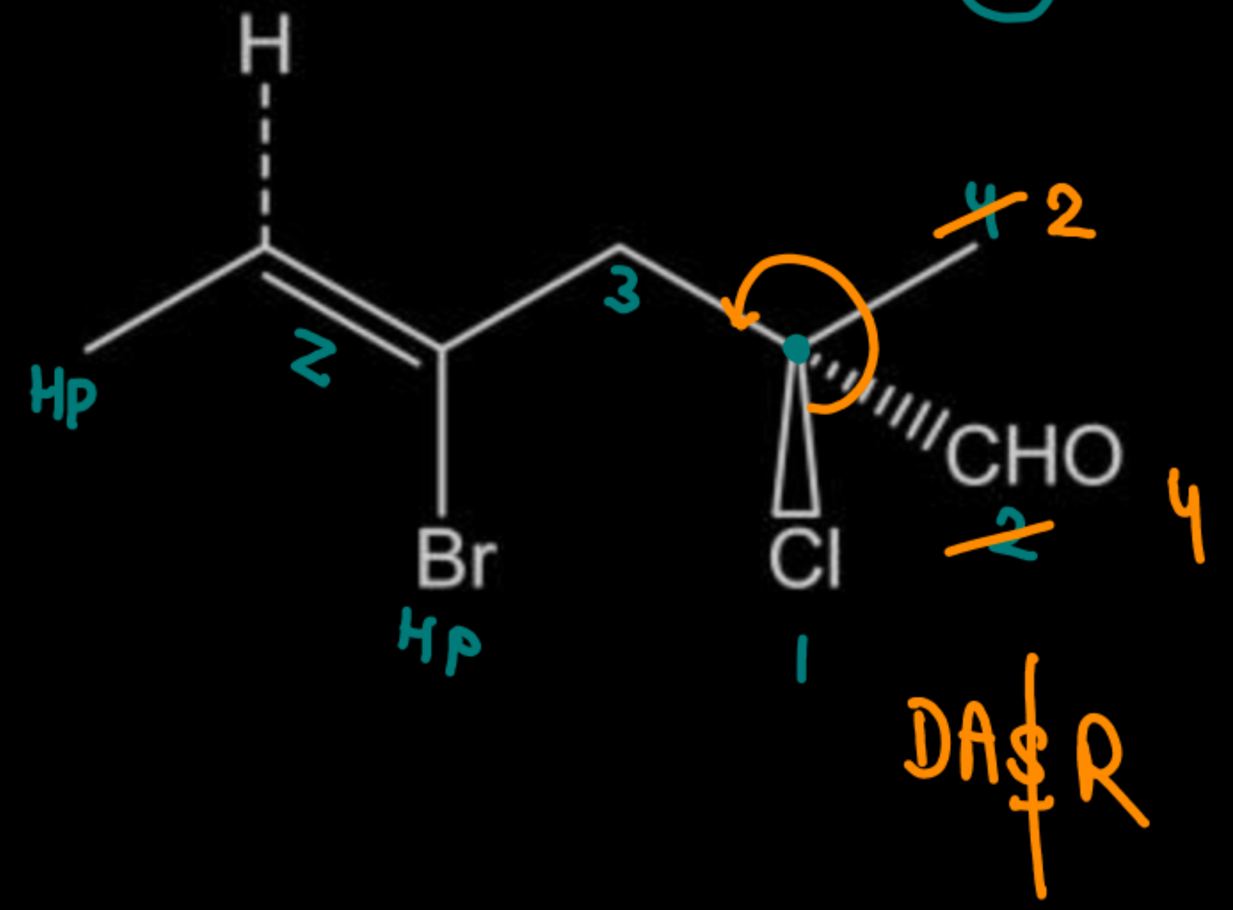
3
CH3
1
HO
HOOC
H
2
4



3
CH3
1
HO
C
H
COOH
4
2

DAS R

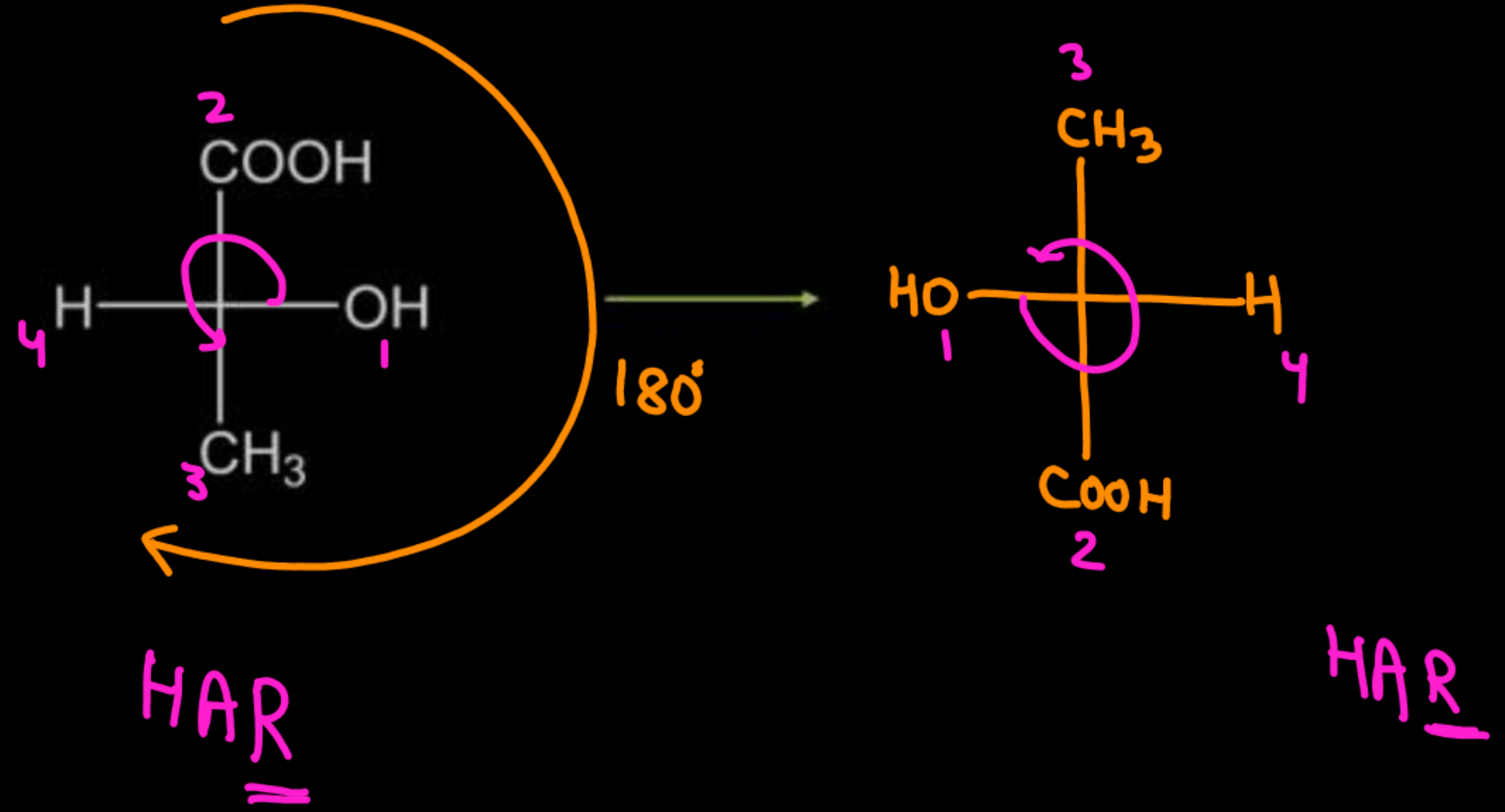

H
Me
HO
C
C
Br
H₃C
H
DCR
DCR
S


H
Hp
Z
3
Br
Hp
Cl
1
CHO
2
4
DASR

Some Important Points

1: If Fischer is rotated by 180° in plane of paper then it is homomer or identical.

both have same configuration.

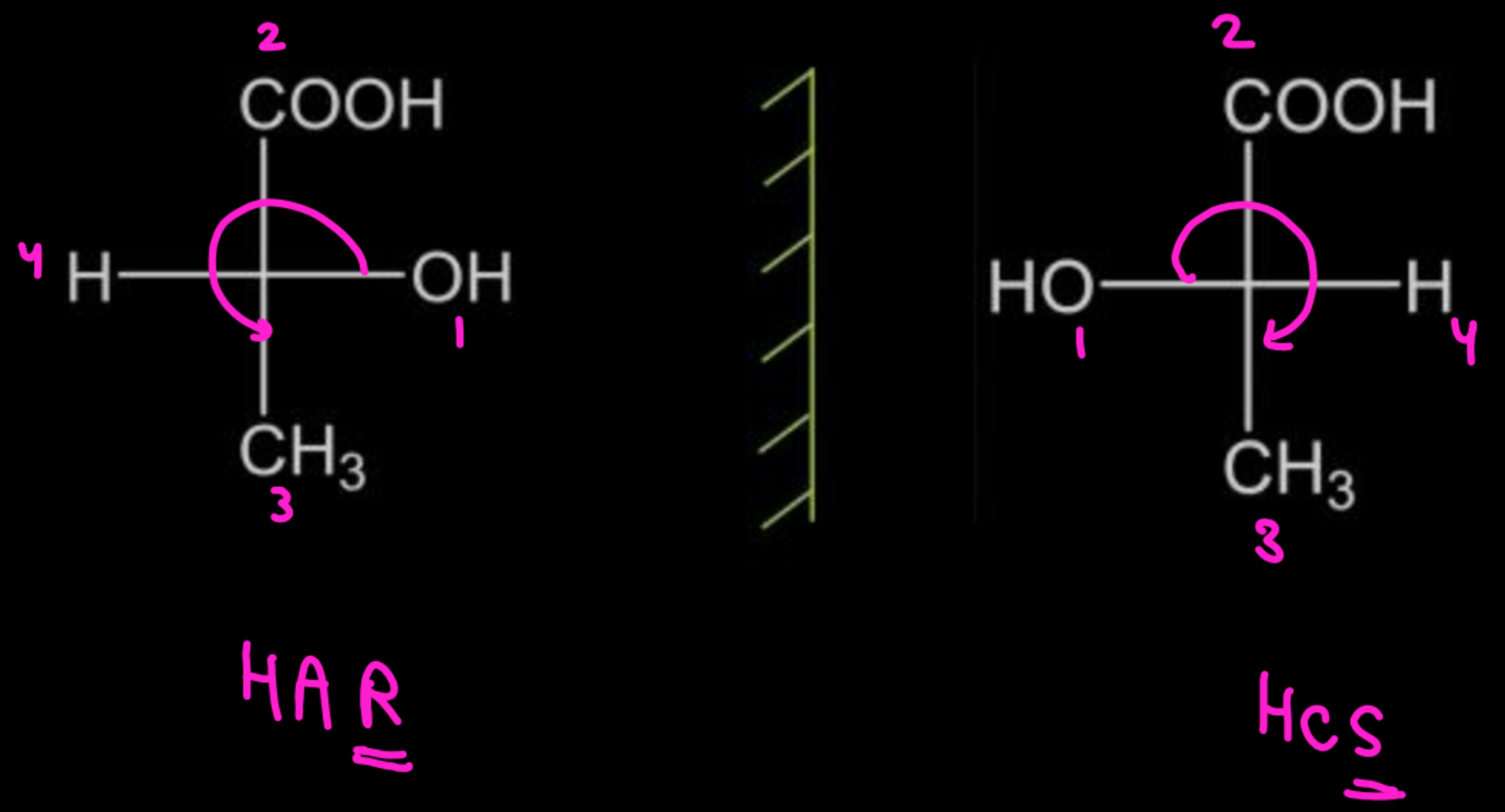


2: If Fischer is rotated by 180° by lifting it from plane of paper then new fischer formed will be mirror image of previous fischer.

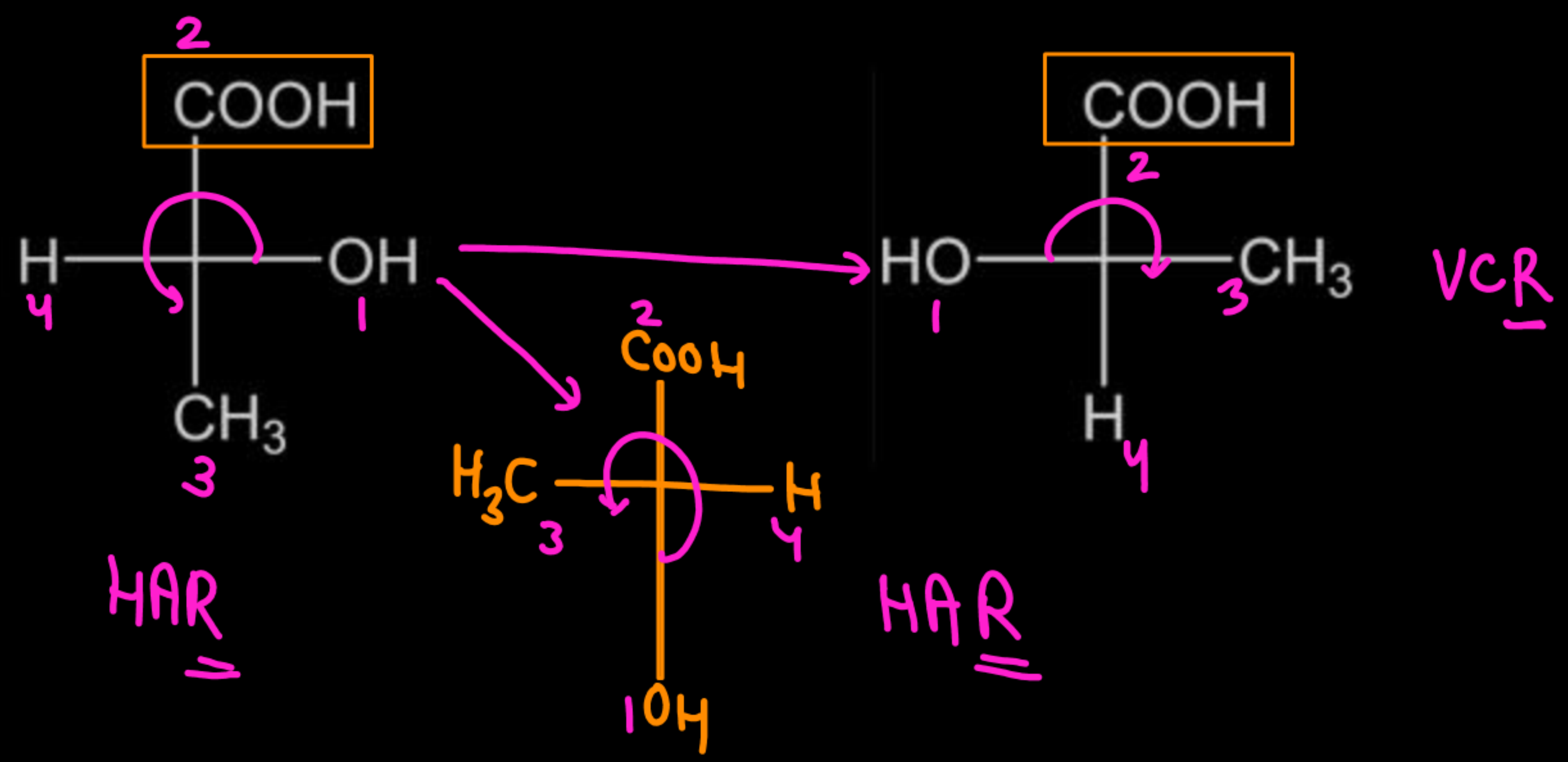
Configuration is opposite

R → S

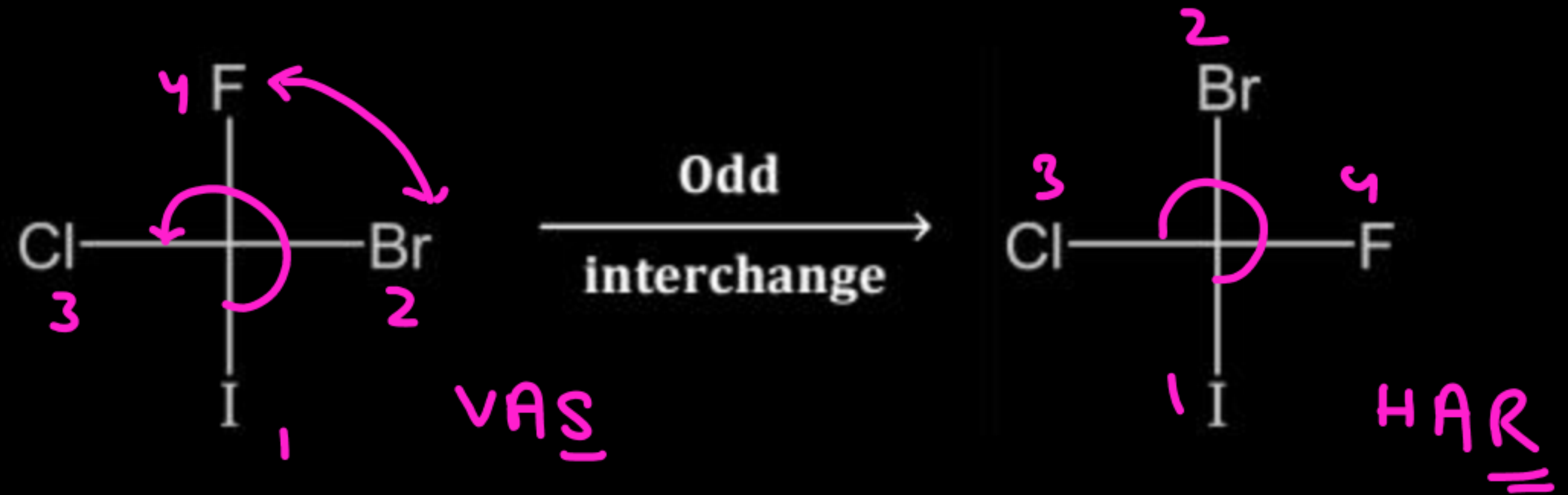
S → R

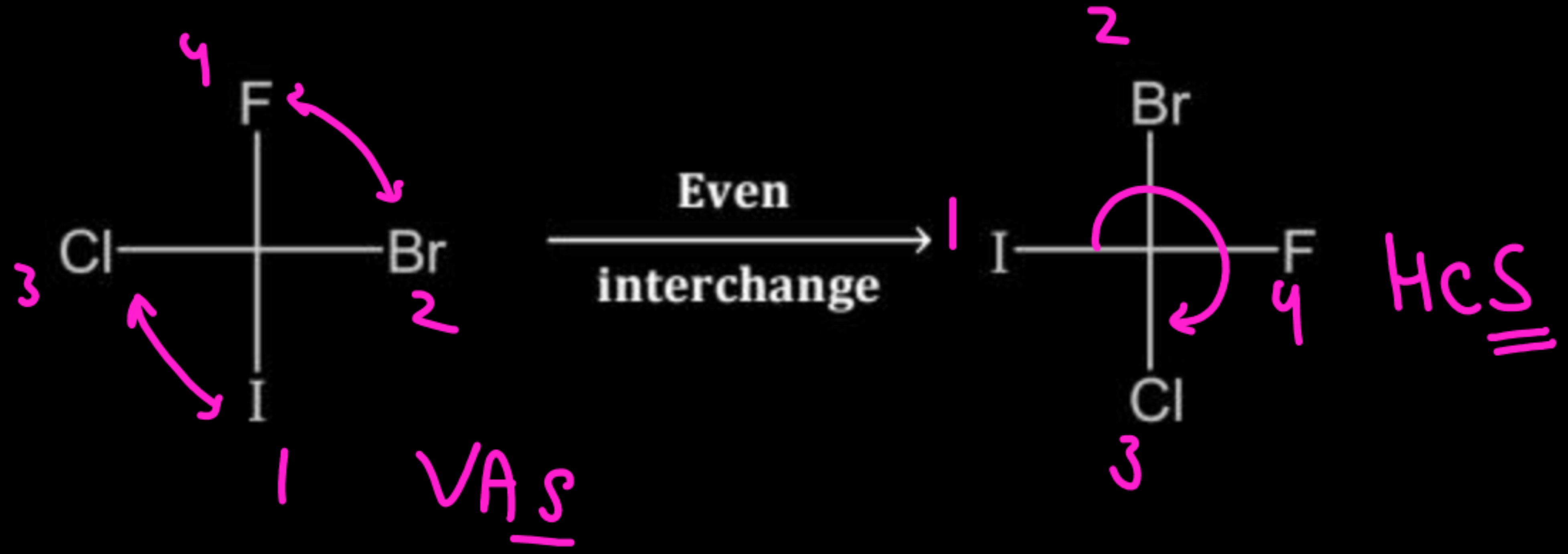


3: If any one group is fixed and remaining 3 groups is rotated clockwise or anti-clockwise then configuration will remain same (applicable for both fischer as well as wedge-dash).



4: Odd number of interchange of group around a chiral carbon will reverse the configuration but even number of interchange will retain the configuration (applicable for both fischer and wedge-dash).

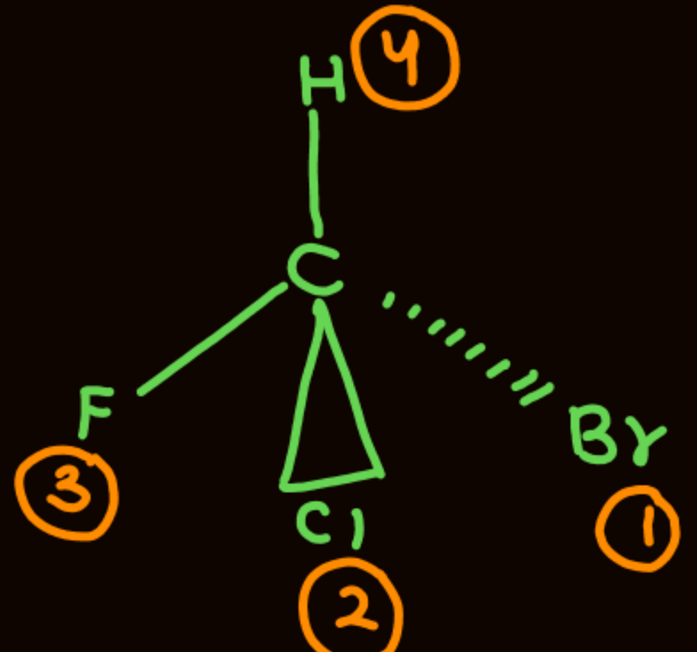




THANK YOU
All the Best!!

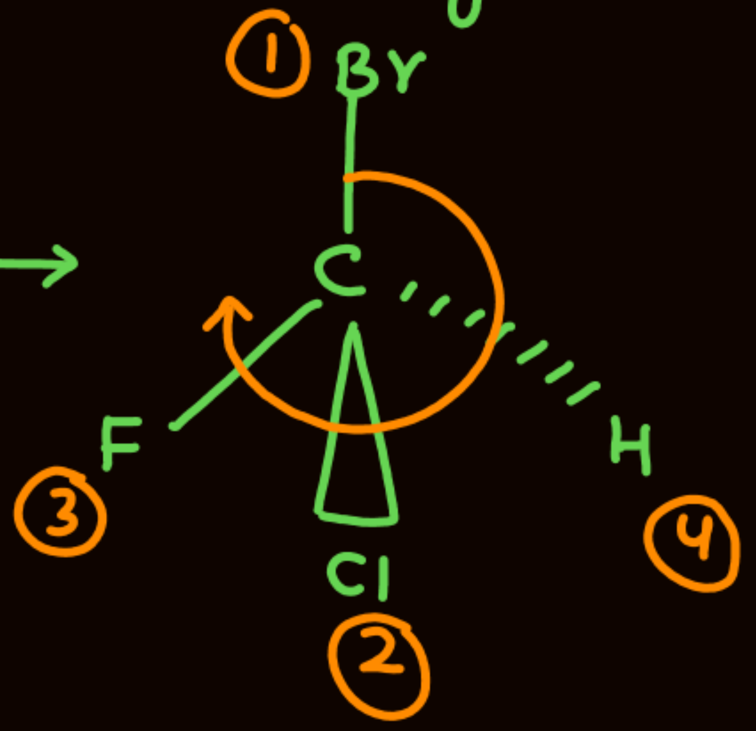
Enantiomer

If comp is Unsymmetrical → Mirror Image is Enantiomer.
(POS & COS absent)
(configuration is opposite)



Comp 1

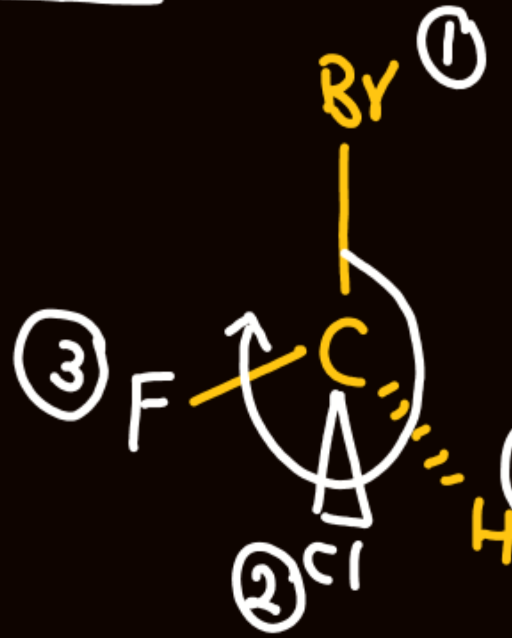
→



DCR

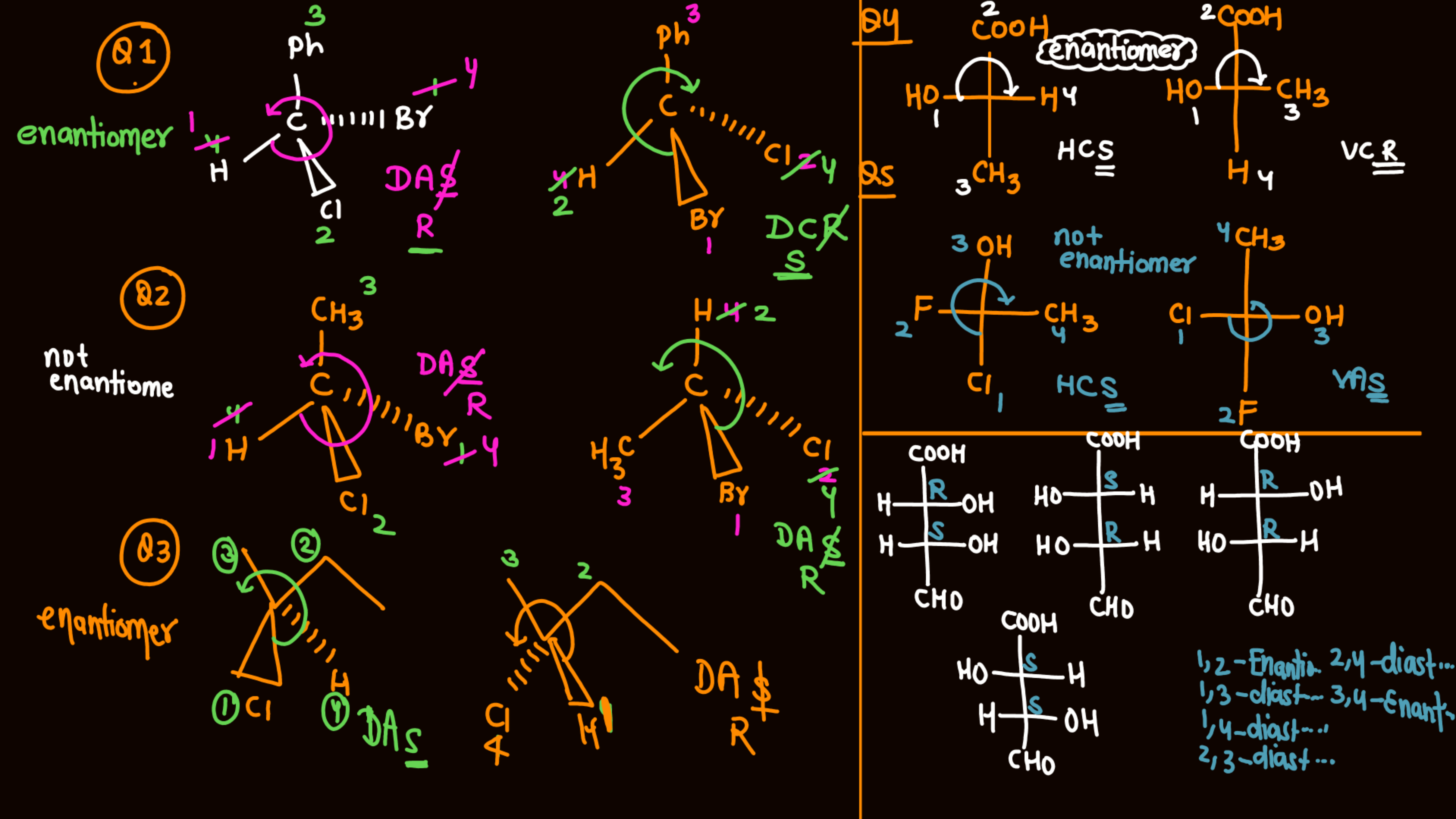
S

* Comp 1 & comp 2 are enantiomers.



DCR

comp 2


Q1
enantiomer
Ph
C
Br
H
Cl
DAS
R
Ph
C
Cl
H
Br
DCR
S
Q2
not
enantiome
CH3
C
Br
H
Cl
DAS
R
H
C
H3C
Cl
Br
DAS
R
Q3
enantiomer
Cl
H
DAS
Cl
H
DAS
R
Q4
COOH
HO
H
CH3
enantiomer
COOH
HO
CH3
H
HCS
VCR
Q5
OH
F
CH3
Cl
not
enantiomer
CH3
Cl
OH
F
HCS
VAS
COOH
H
OH
H
OH
CHO
R
S
COOH
HO
H
HO
H
CHO
S
R
COOH
H
OH
HO
H
CHO
R
R
COOH
HO
H
H
OH
CHO
S
S
1,2-Enantio.. 2,4-diast...
1,3-diast... 3,4-Enant..
1,4-diast...
2,3-diast...

note → Unsymmetrical Comp → Complete change in Configuration → Enantiomer (non superimposable mirror image)

↓ no pos & no cos

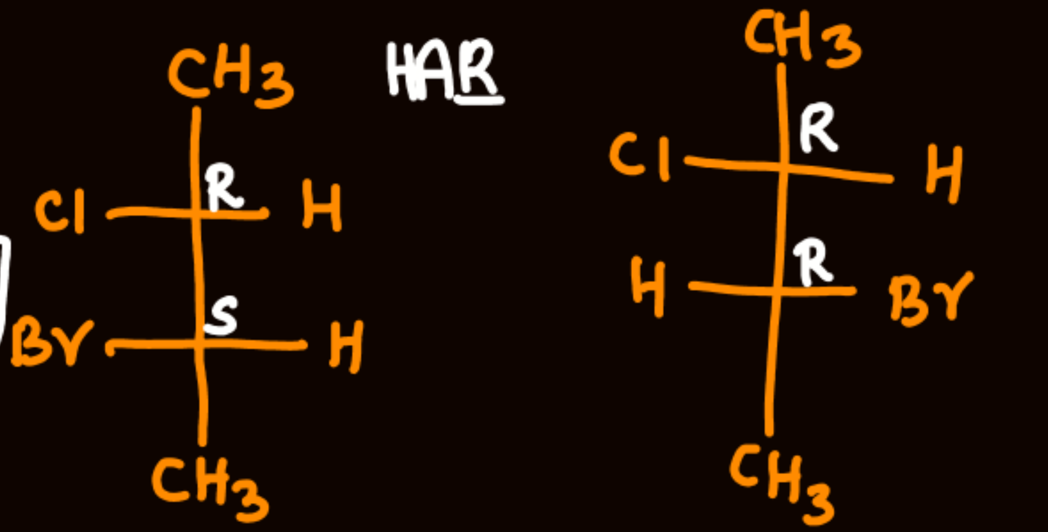
Symmetrical comp → Complete change in configuration → identical comp (superimposable mirror image)

↓ either Pos or cos or both present

Unsymmetrical comp → Partial change in Configuration → Diastereomers (These are not mirror image)

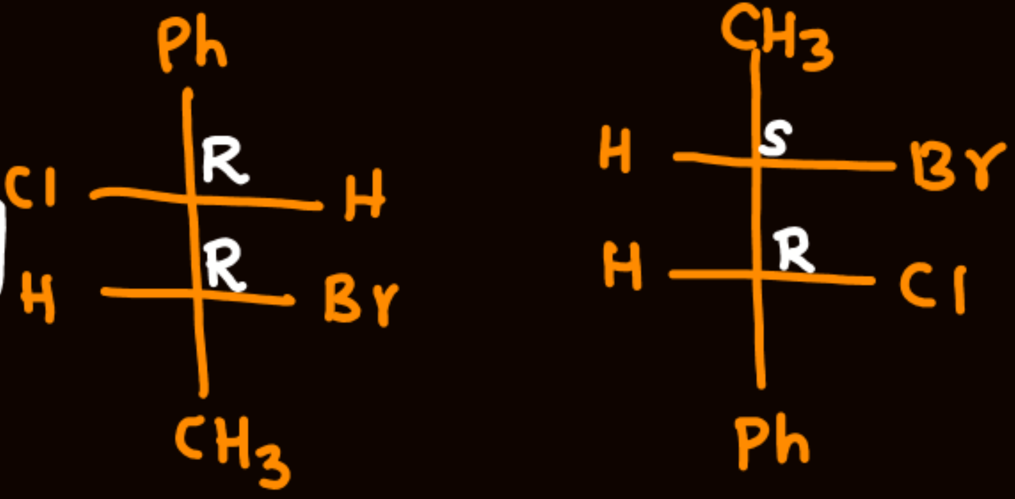
Q

diasteromer



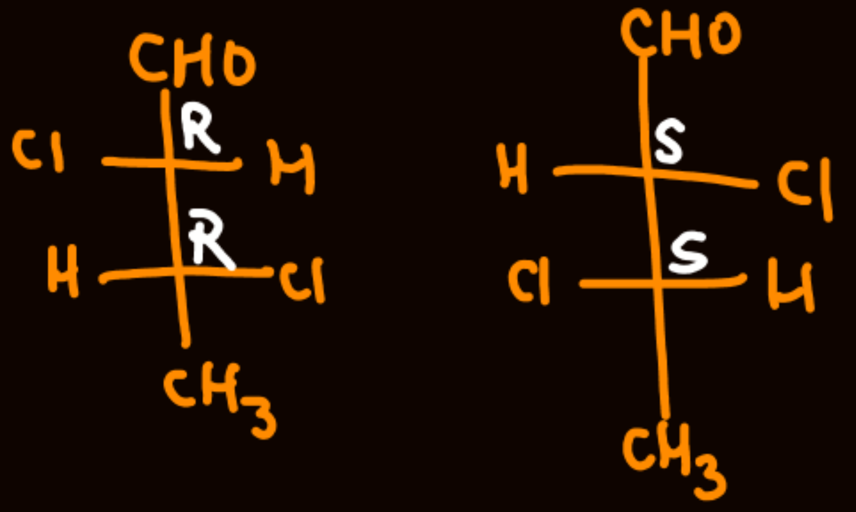
Q

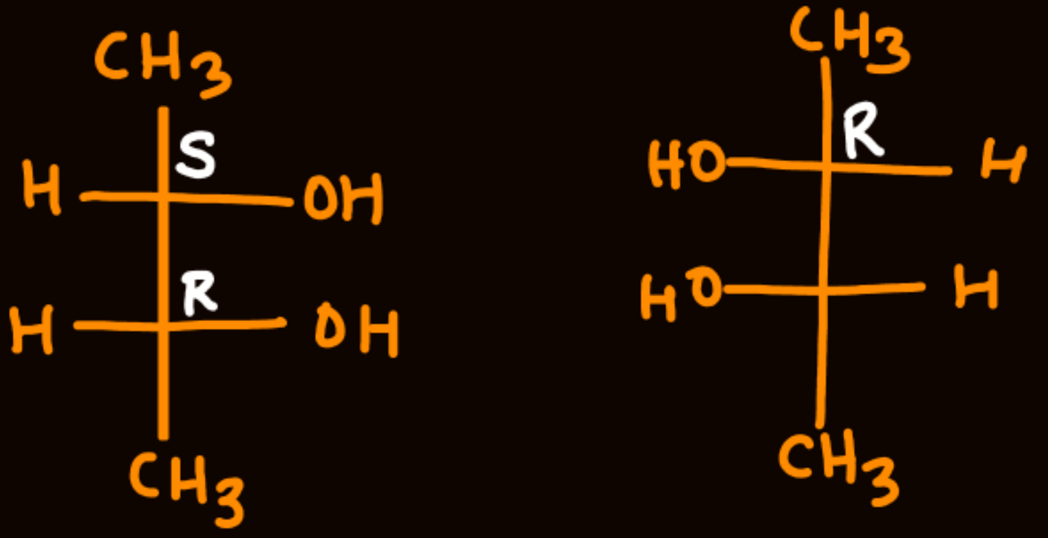
diastereomer



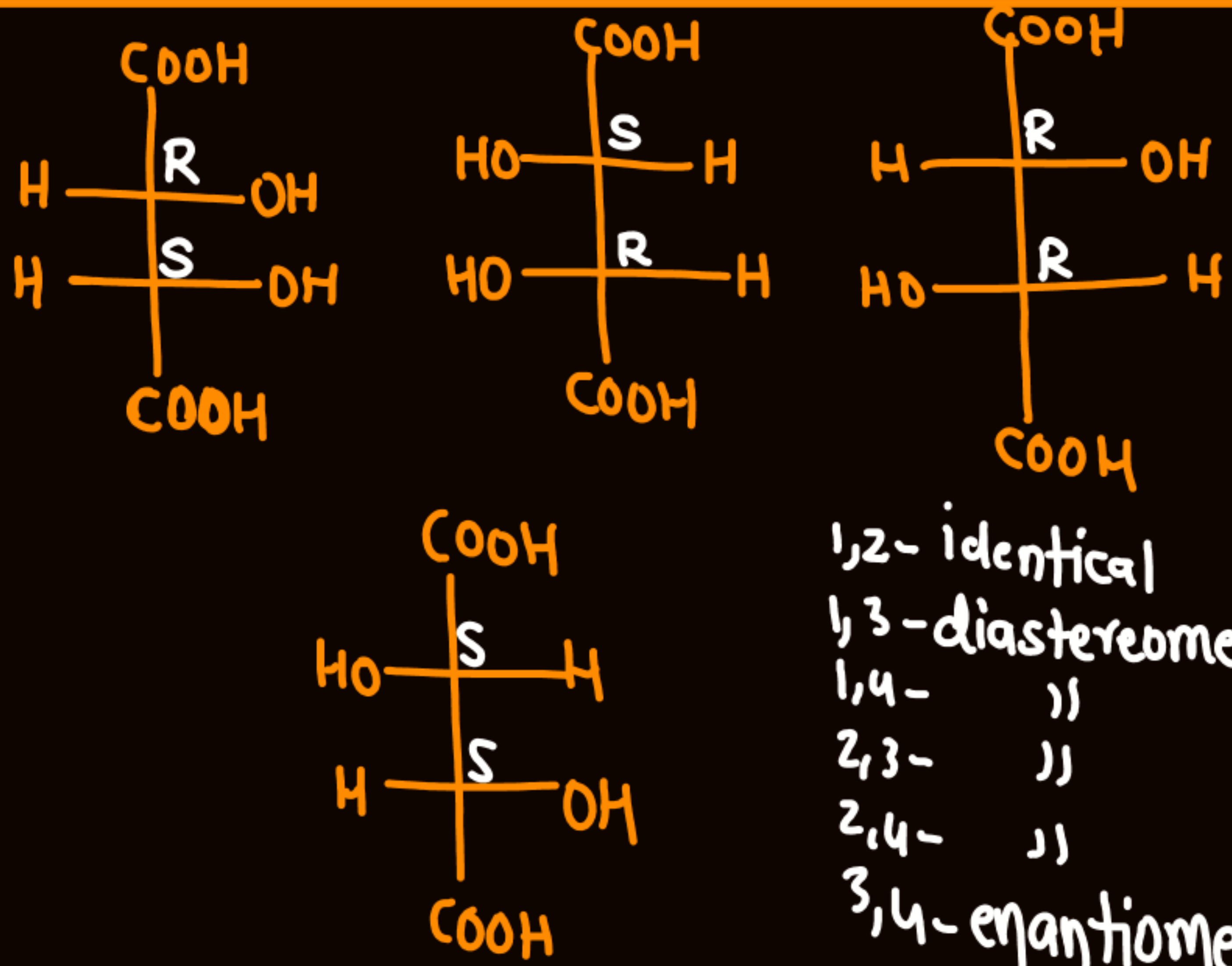
Q

Enantiomer





identical



1,2- identical
1,3-diastereomer
1,4- "
2,3- "
2,4- "
3,4- enantiomer ✓

Mesocompound

optically inactive Compound, having more than one chiral center.

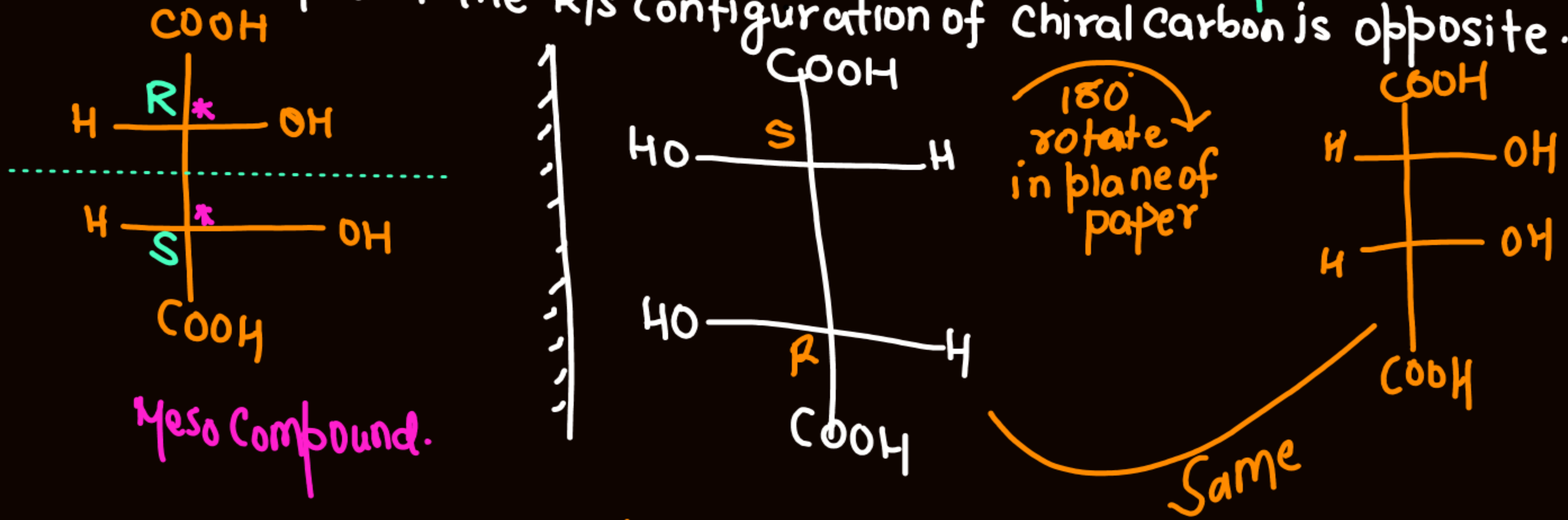
↓ symmetrical

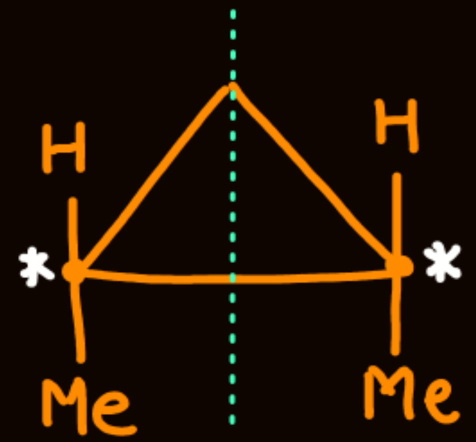
↓ Pos/cos/both present

Mirror image of Meso comp is identical.

Meso compounds are optically inactive due to internal compensation.

In meso Compound the R/s configuration of Chiral Carbon is opposite.

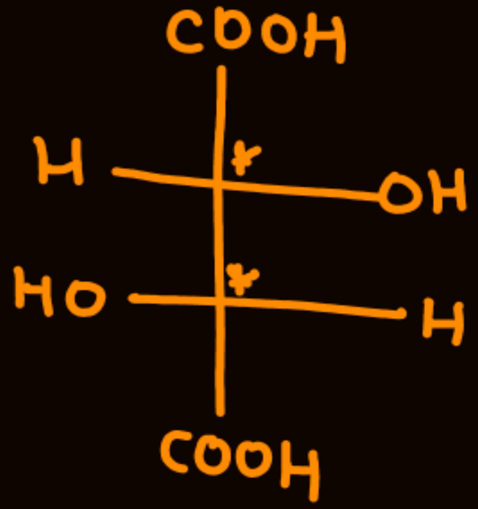


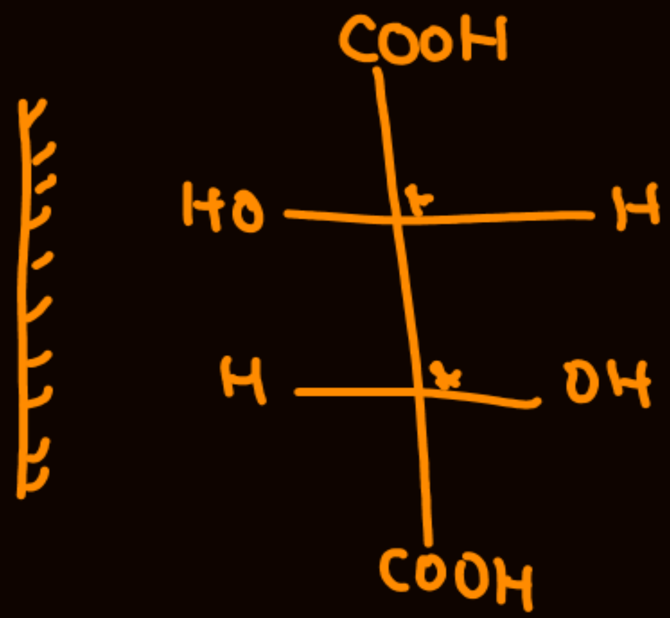


2 chiral center ✓

POS ✓

Meso ✓





} Enantiomer

2 chiral ✓

POS ✗

COS ✗

Meso ✗

Racemic Mixture

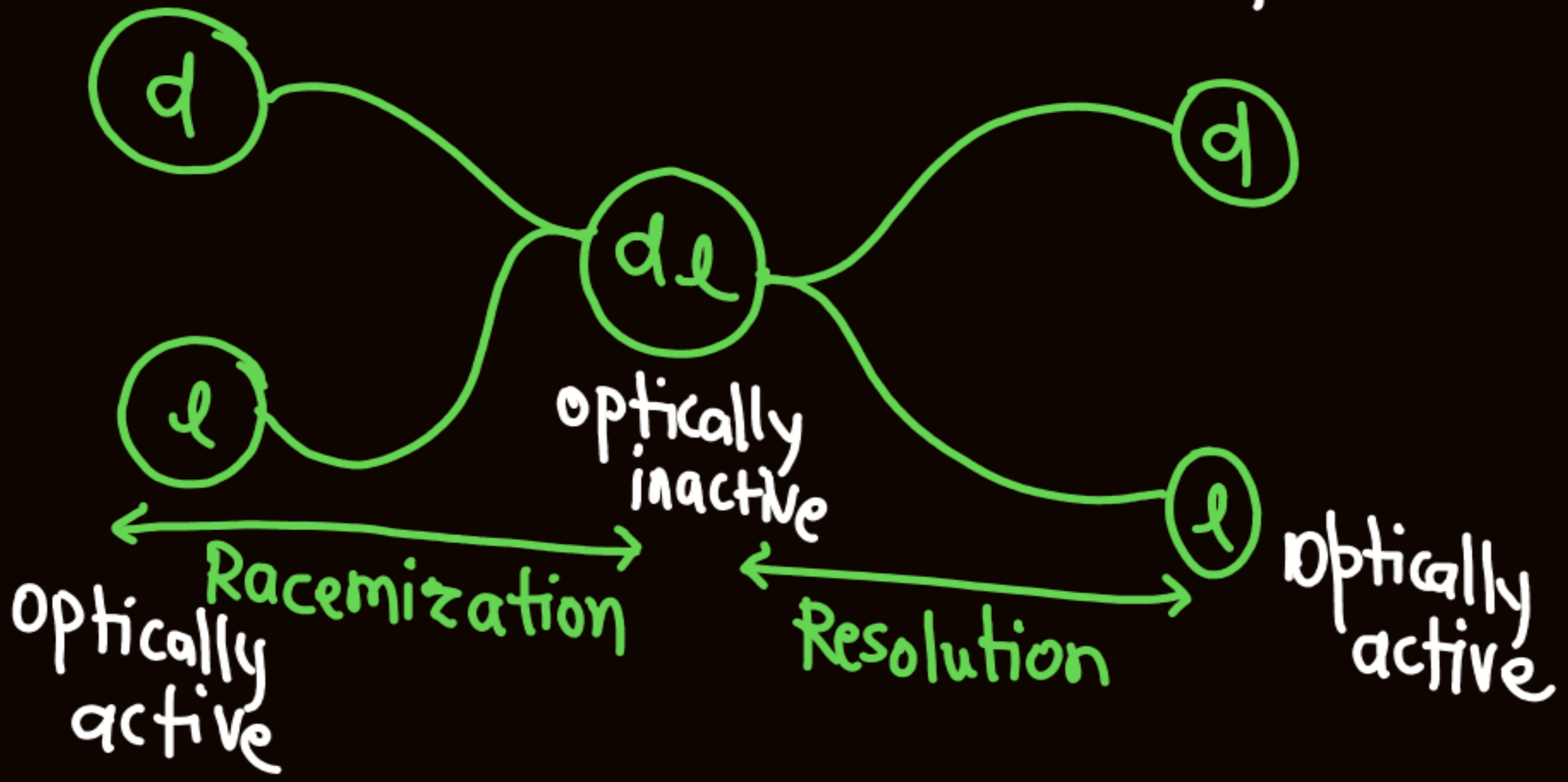
\# Equimolar mixture of d & l enantiomer is called Racemic Mixture.

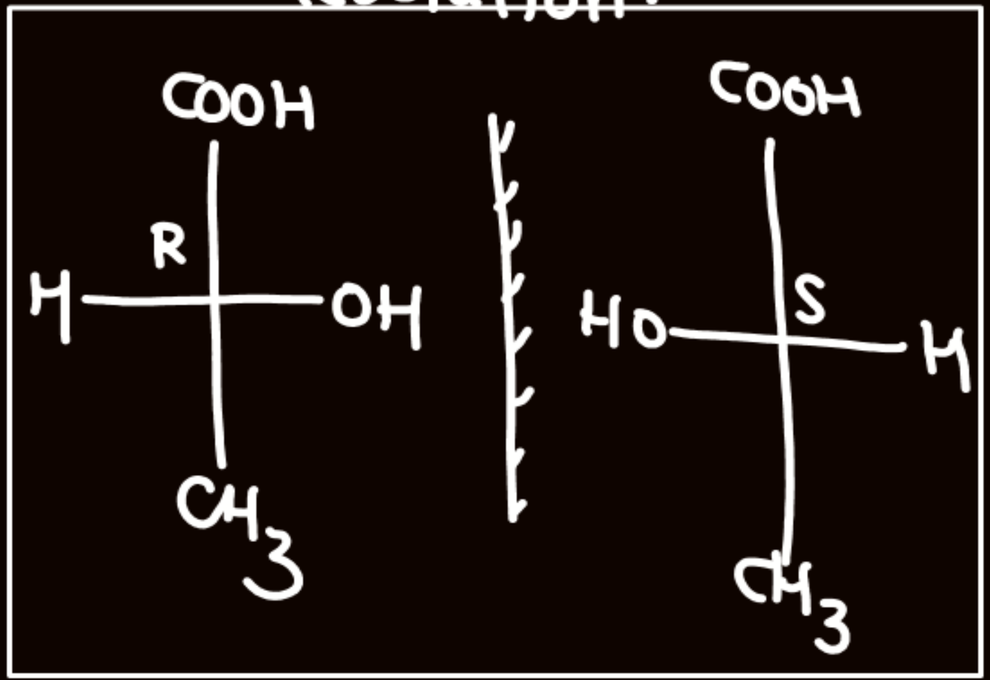
50% d + 50% l

optically inactive due to External Compensation.

\# process of formation of Racemic mixture ⟶ Racemization.

\# process of separation of d & l enantiomer from Racemic mix → Resolution.





D & L configuration

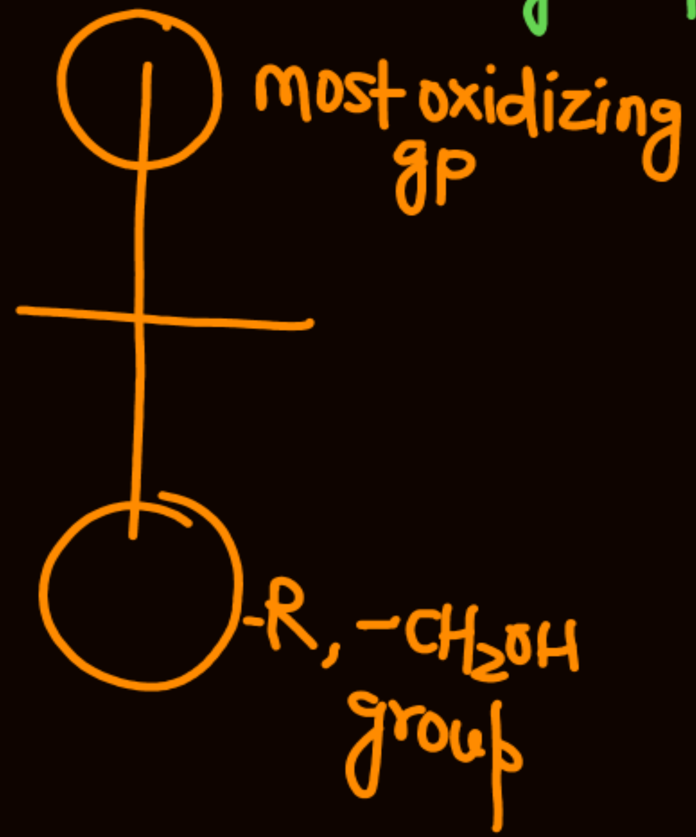
→ Fischer Projection

→ Carbohydrate & Amino acid

More oxidising group should lie at the top of fischer projection.

↳ $-COOH$, $-CHO$ etc

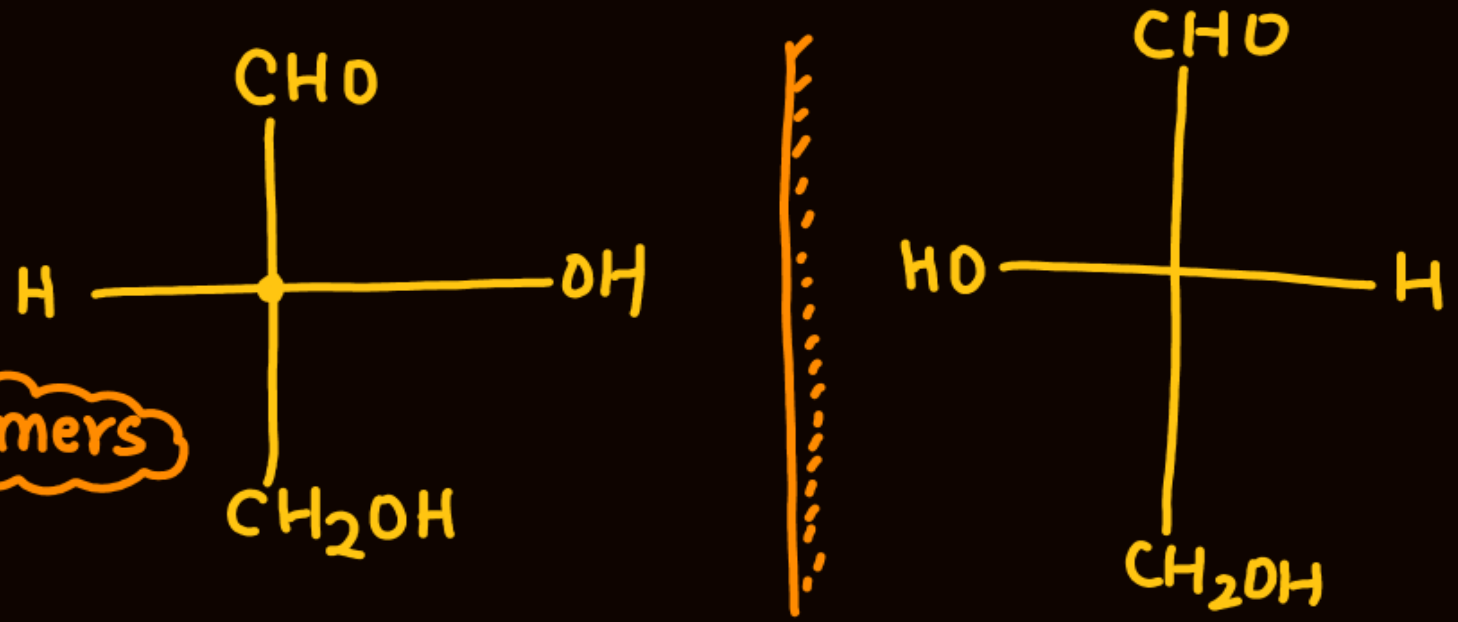
$-R$, and $-CH_2-OH$ group should lie at the bottom of fischer projection.



OH/NH_2 → RHS → D

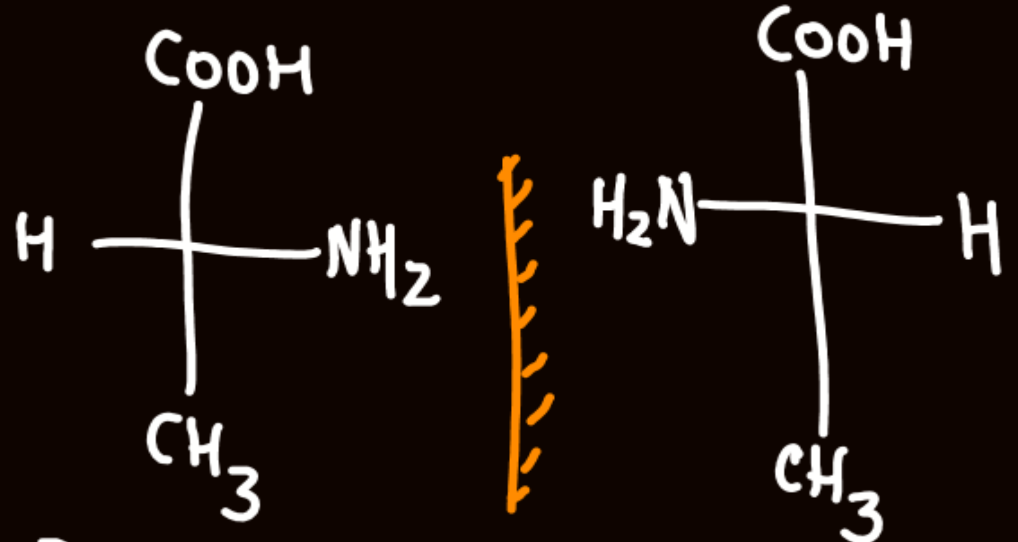
OH|NH_2 → LHS → L

enantiomers

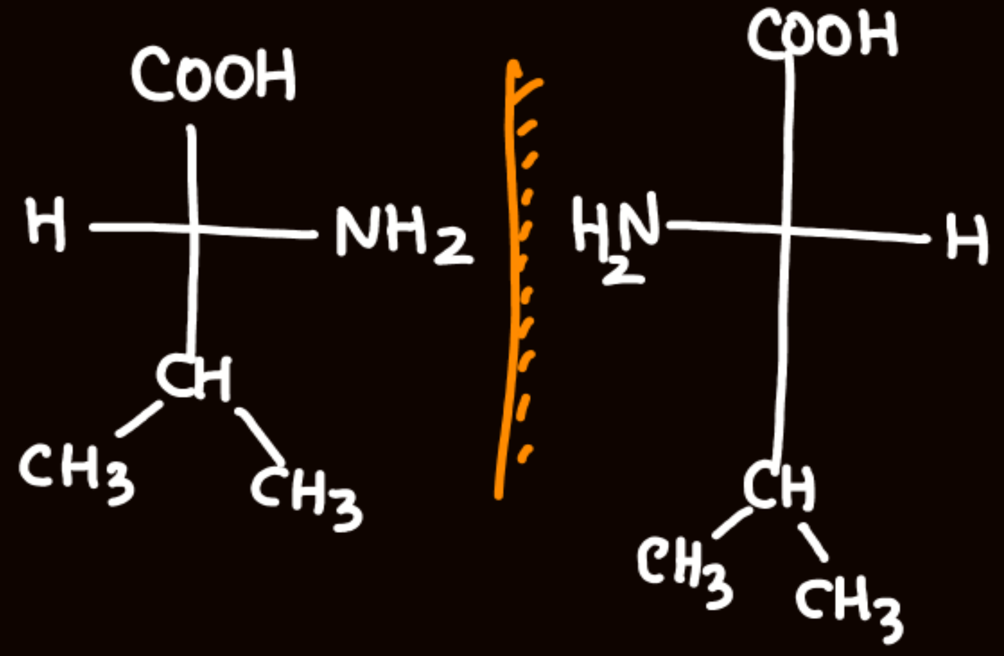


D-Glyceraldehyde L-Glyceraldehyde

enantiomer

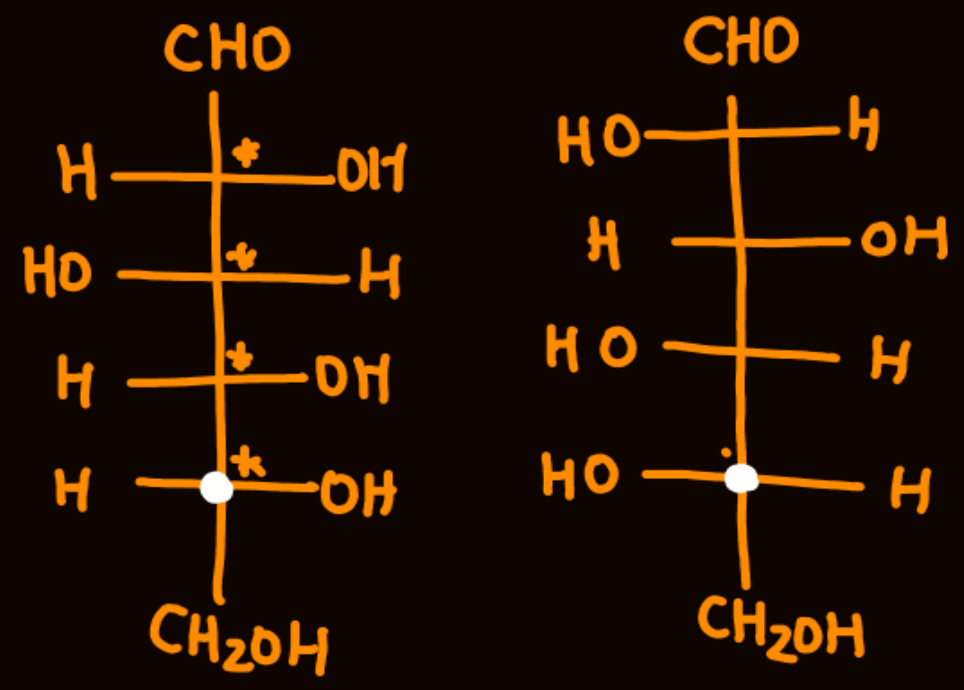


D-Alanine L→Alanine



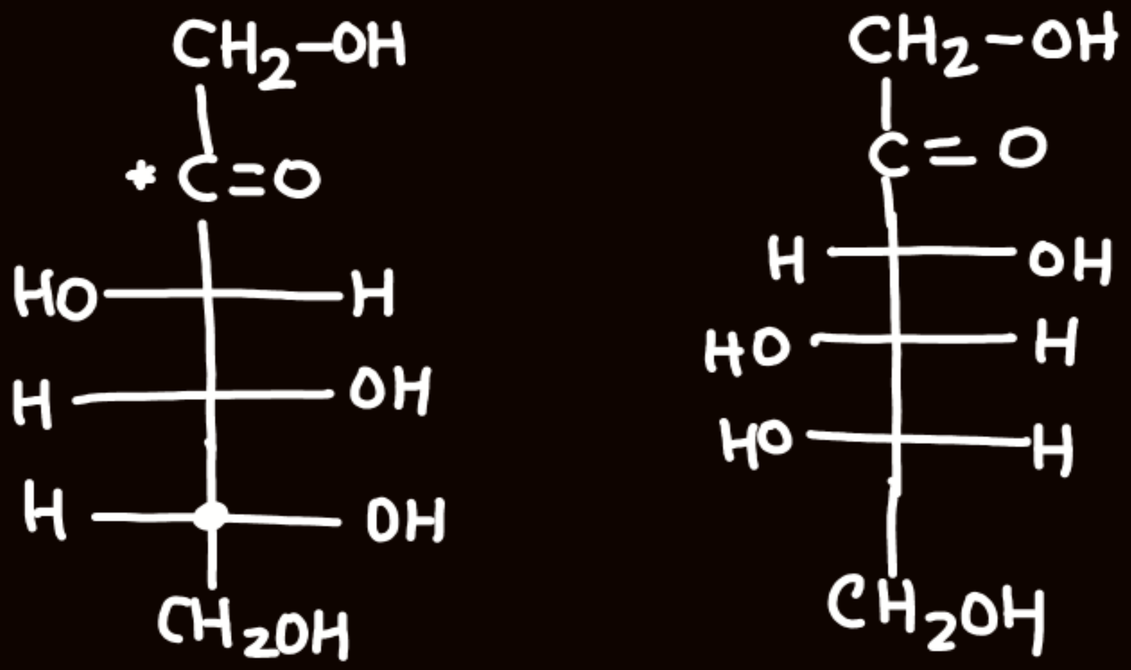
D-Valine L-Valine

enantiomer



D-Glucose L-Glucose

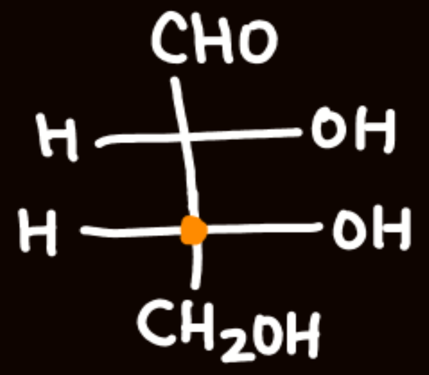
Enantiomer



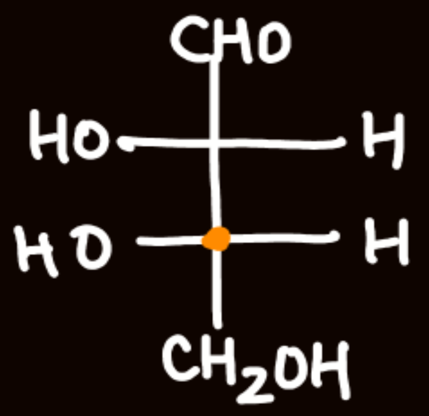
D Fructose L-Fructose

Enantiomer

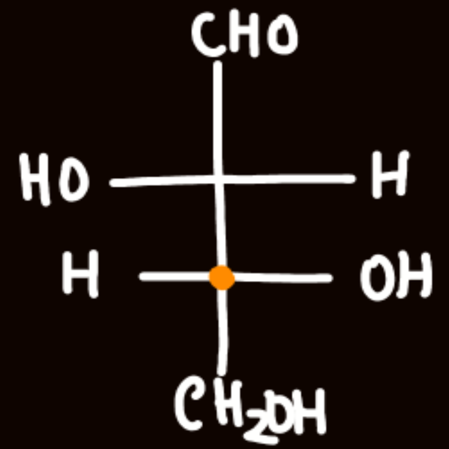
neet 2016



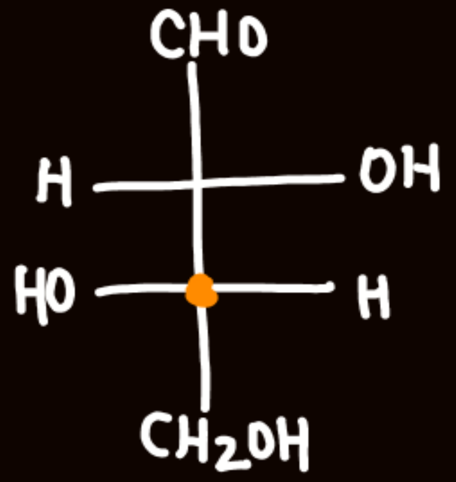
D-erythrose



L-erythrose

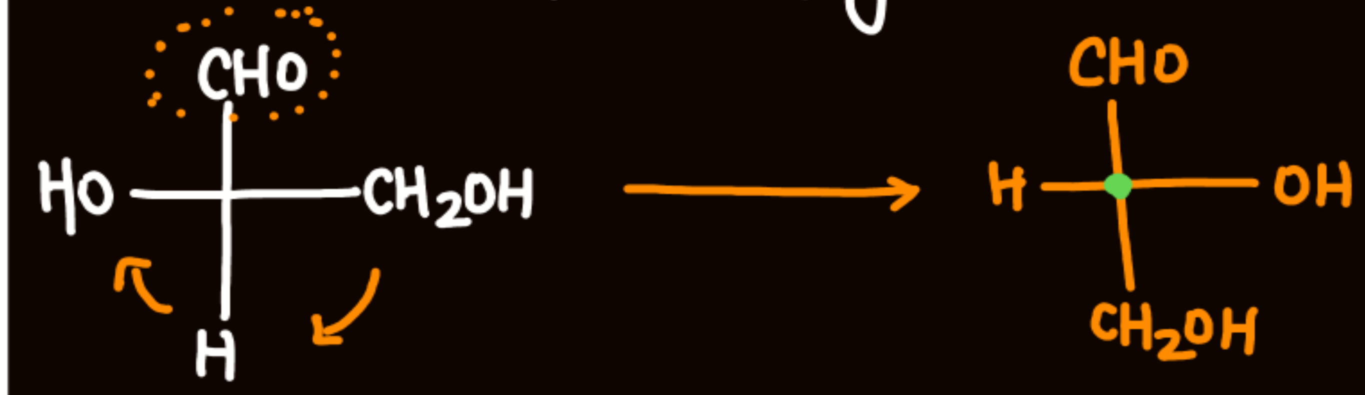


D-Threose



L-Threose

Que Find D/L Configuration–



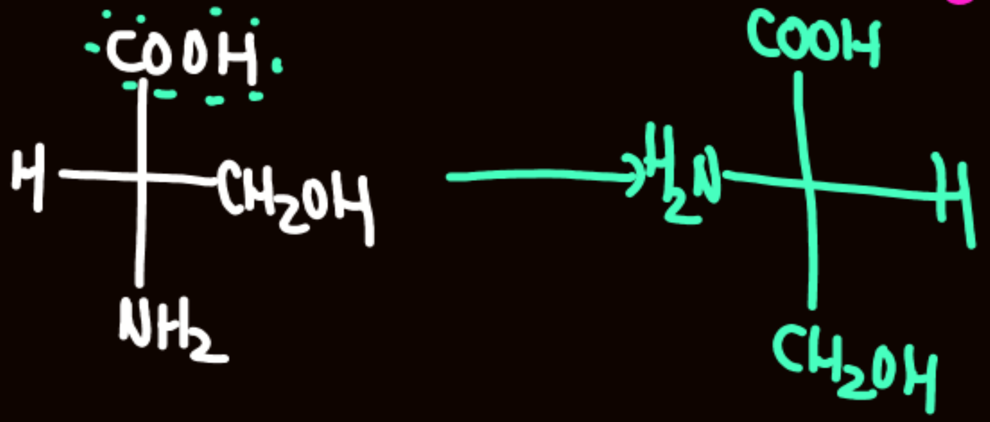
(D)



(L)



(L)



(L)

* Special case → Spiro / Cummulene / Biphenyl

Counting of optical isomers.

Counting of stereoisomers.

Counting of isomers.

Special Cases

Isomerism

1. cummulene Comp / Cummulated polyene
2. Spiro Comp
3. Biphenyl Comp & ortho Substituted Biphenyl Comp

Cummulene/cummulated Polyene

even: $\overset{sp^2}{CH_2} \overset{H}{=} \overset{sp}{C} \overset{V}{=} \overset{sp^2}{CH_2}$ (Allene) — Vt, Hz

odd: $CH_2 \overset{H}{=} C \overset{V}{=} C \overset{H}{=} CH_2$ — V, V (Hz)

even: $CH_2 \overset{H}{=} C \overset{V}{=} C \overset{H}{=} C \overset{V}{=} CH_2$ — V, H

odd: $CH_2 \overset{H}{=} C \overset{V}{=} C \overset{H}{=} C \overset{V}{=} C \overset{H}{=} CH_2$ — V, V

even: $CH_2 \overset{H}{=} C \overset{V}{=} C \overset{H}{=} C \overset{V}{=} C \overset{H}{=} C \overset{V}{=} CH_2$ — V, H

odd: $CH_2 \overset{H}{=} C \overset{V}{=} C \overset{H}{=} C \overset{V}{=} C \overset{H}{=} C \overset{V}{=} C \overset{H}{=} CH_2$ — V, V

$CH_2 \overset{Hz}{=} C \overset{Vt}{=} C \overset{Hz}{=} C \overset{Vt}{=} C \overset{Hz}{=} CH_2$

sp^2 sp sp sp sp sp^2

P_x, P_y — P_x — P_x — P_x — P_x

P_z — P_z

P_y — P_y

P_z — P_z

P_y — P_y

P_z — P_z

even cummulene → Terminal bonds → Diff Plane

odd cummulene → Terminal bond → Same plane

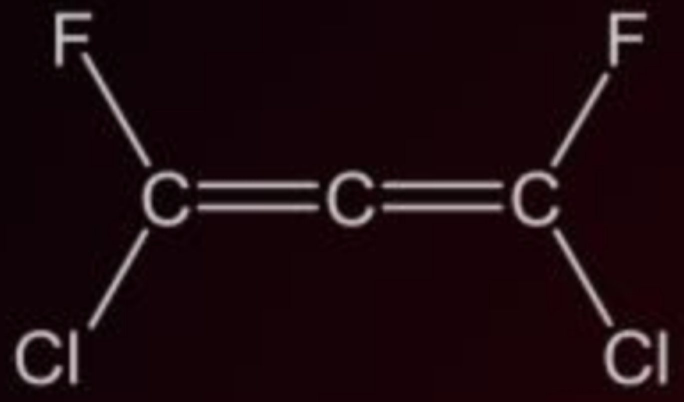
even cummulene → GIX → aerial distance same.

odd " → OIX → pos/cos present.

DOG
- D ↓ Diff Terminal bonds
- O → Odd Cummulene
- G → GI show

D E O
- D ↓ diff. Terminal bond
- E ↓ even cummulene
- O ↓ OI show

Eg1

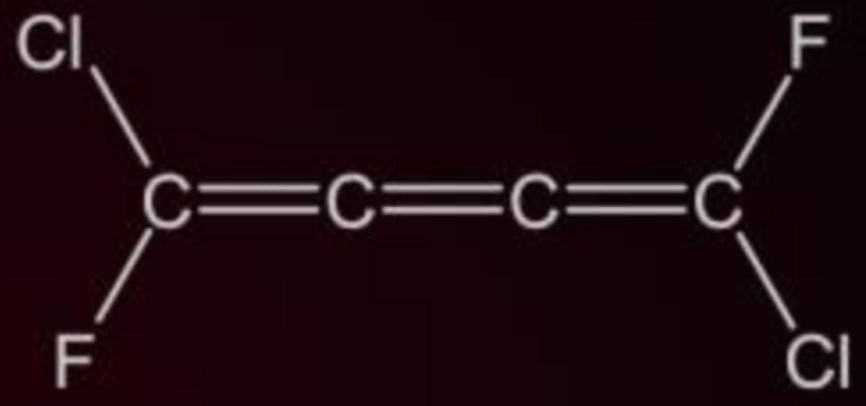


DEO

OI show

optical Isomerism

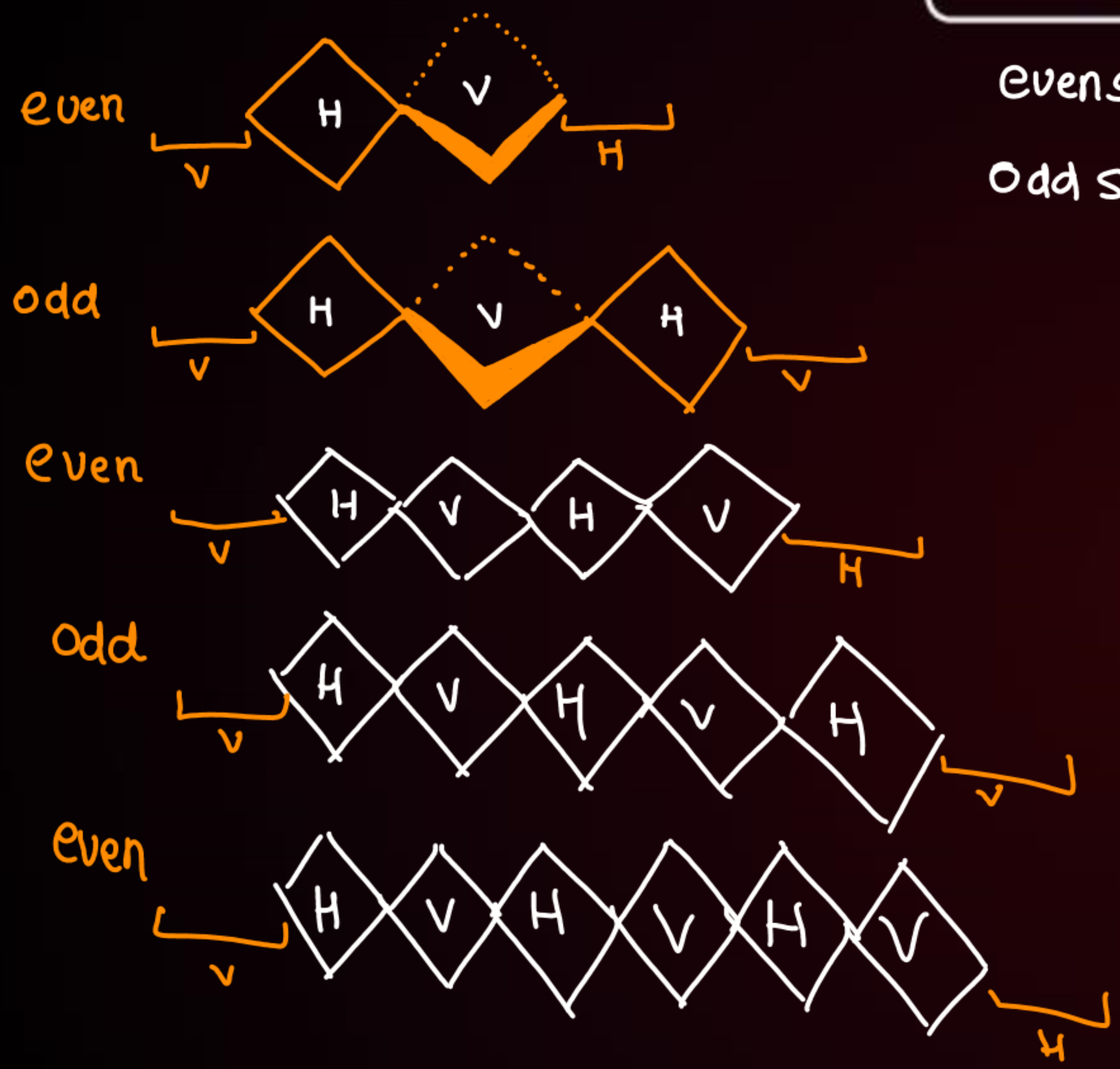
Eg2



DOG

GI show

Spiro



evenspiro → Terminal bonds → Diff Plane.

Odd spiro → Terminal bonds → Same plane.

DOG

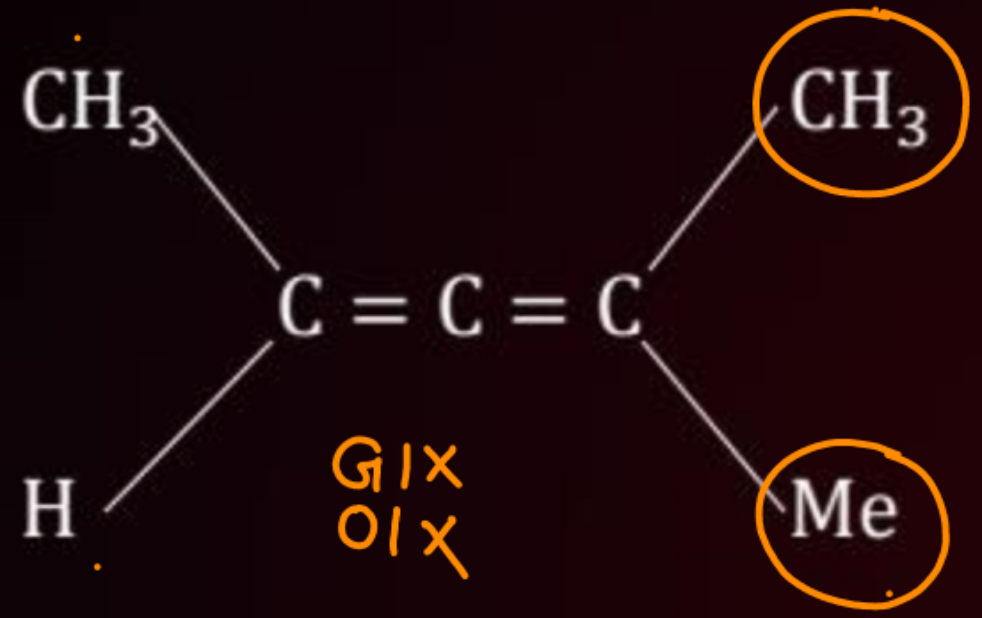
DEO

Summary (Special Case)

	Even	Odd
Same Terminal bond	GI ✗ OI ✗	GI ✗ OI ✗
Diff Terminal bond	DEO OI ✓ GI ✗	DOG GI ✓ OI ✗

Que. **Find G.I./O.A.I.?**

1\.



2\. $CH_3 - CH = C = CH - CH_3$

DEO OI ✓

3\. $CH_3 - CH = C = C = CH - CH_3$

DOG ✓

4\. $CH_3 - CH = C = CH_2$

G I X
O I X

no chiral
no OI

spiro X
cyclo ✓
GI ✓

5.



6.



DE 0 OI ✓

7.



DOG
✓

8.



GI X
OI X

9.



DEO OI ✓

10.



DOG

11.



Ring → 1chiral → shows OI ✓

Biphenyl

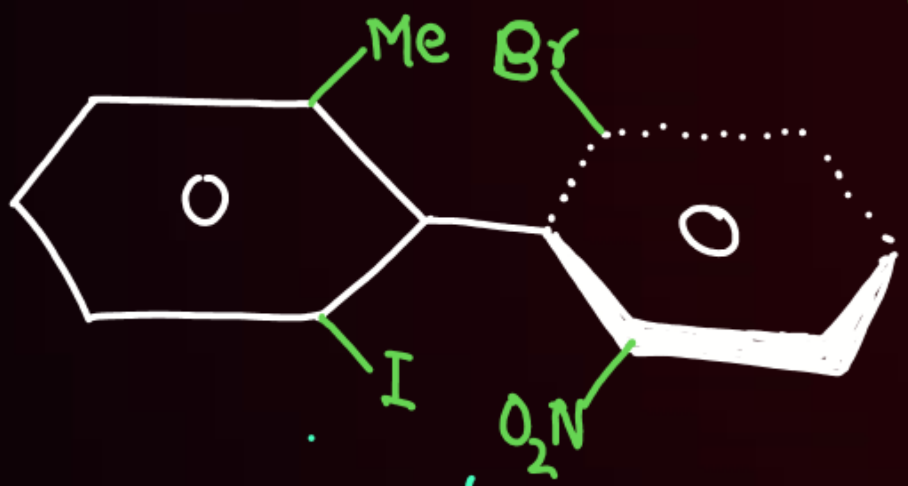


→ Free Rot^n is possible in Biphenyl.

→ never show GI → bcoz for GI → Restricted Rot^n is must

→ never show OI → bcoz slice pos available.

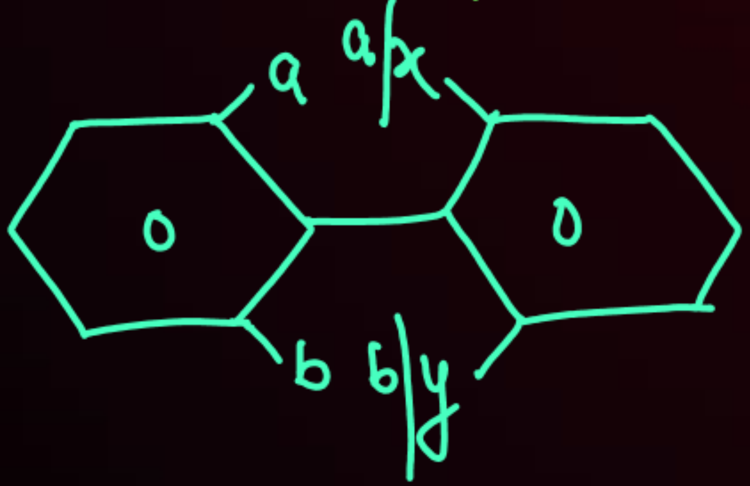
Ortho Substituted Biphenyl



When Bulky group is present at ortho position in Biphenyl Ring. (Repulsion occurs)

To avoid Repulsion → plane changes
↓
never show GI (aerial dist same)

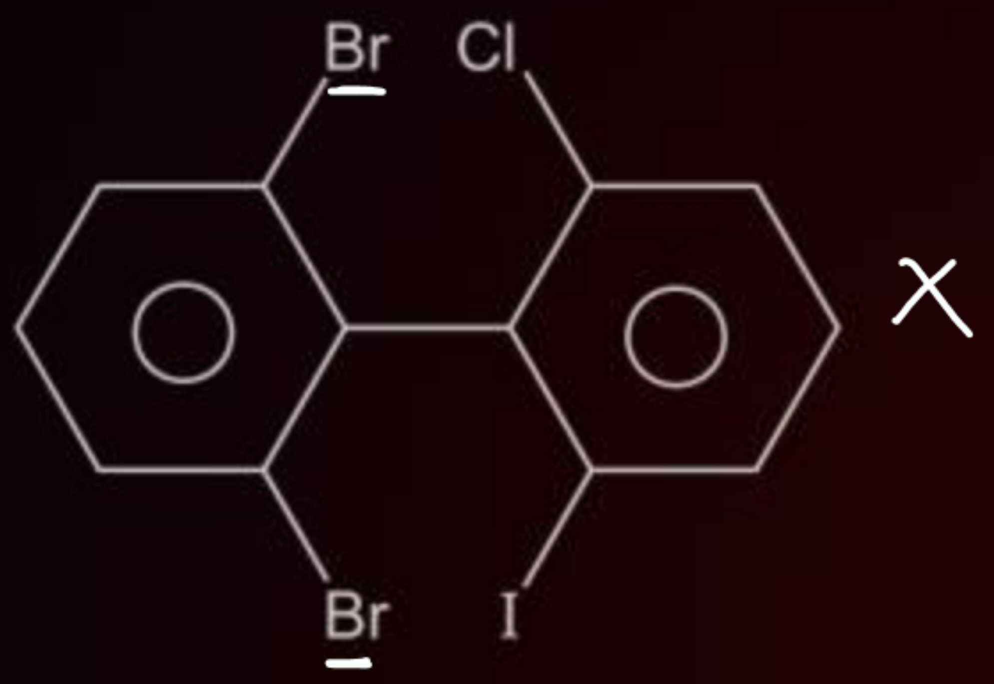
When ortho bonds are different → no pos/no cos
Shows OI ✓

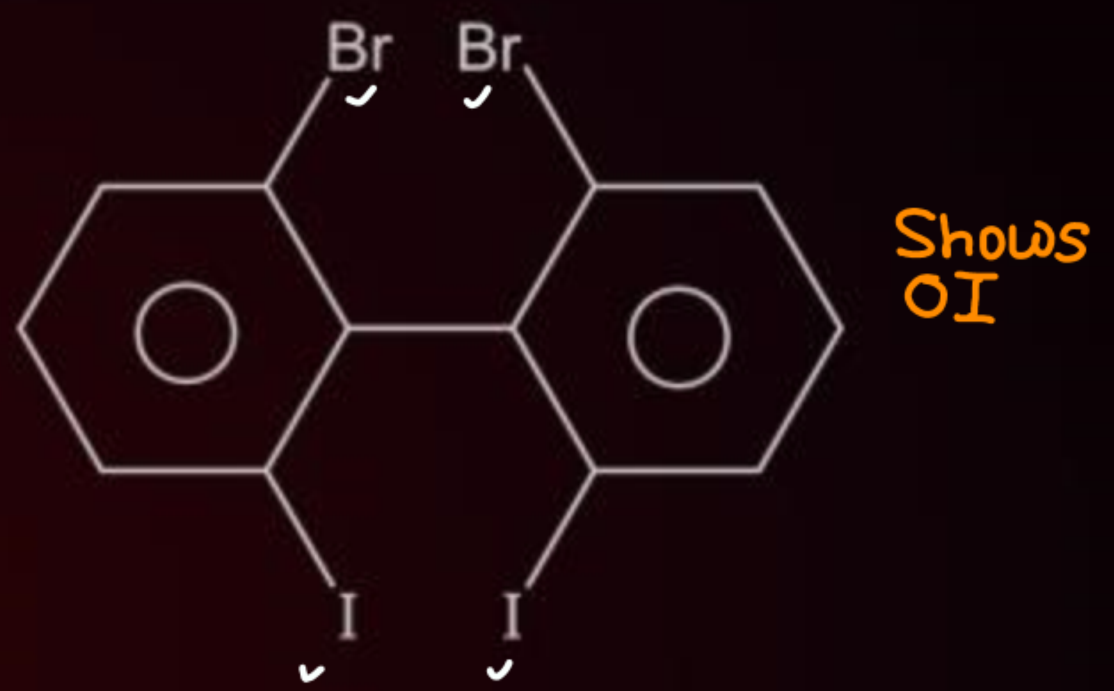


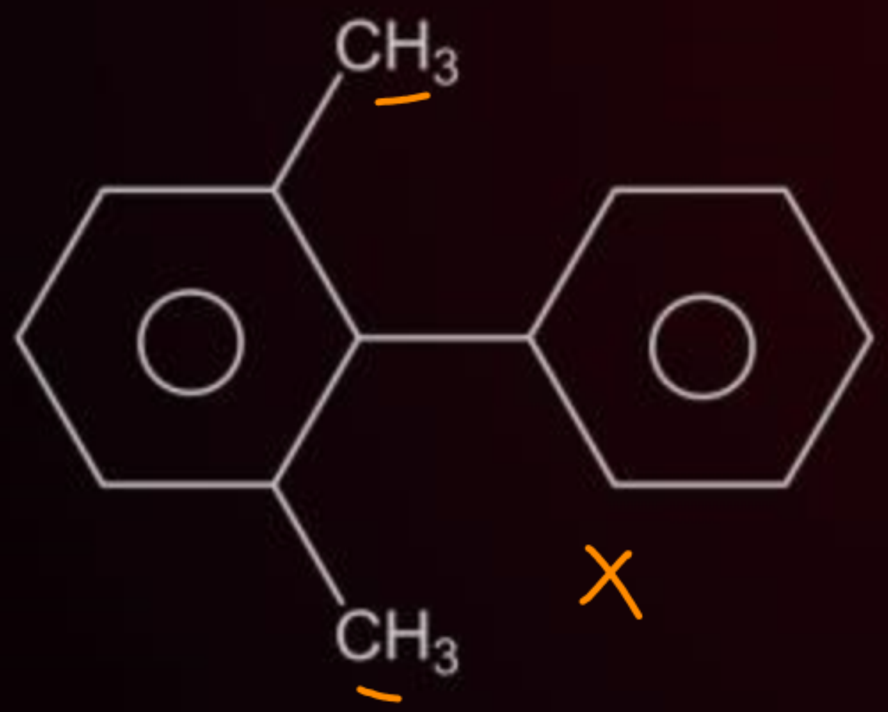
Hulky Group → H | D | T | OH | NH_2 | F | CN

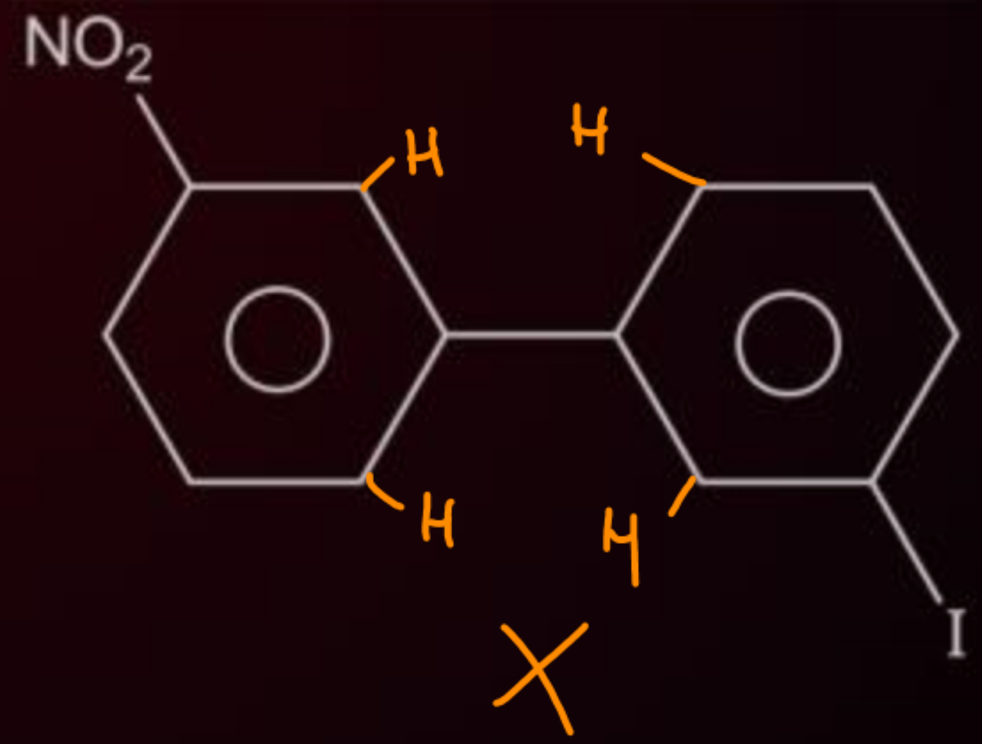
Bulky Group → –R, COOH, –COCl, –$CONH_2$, –CO_2 etc. Cl, Br, I

Que. Which of the following biphenyl compounds is/are chiral/optically active?

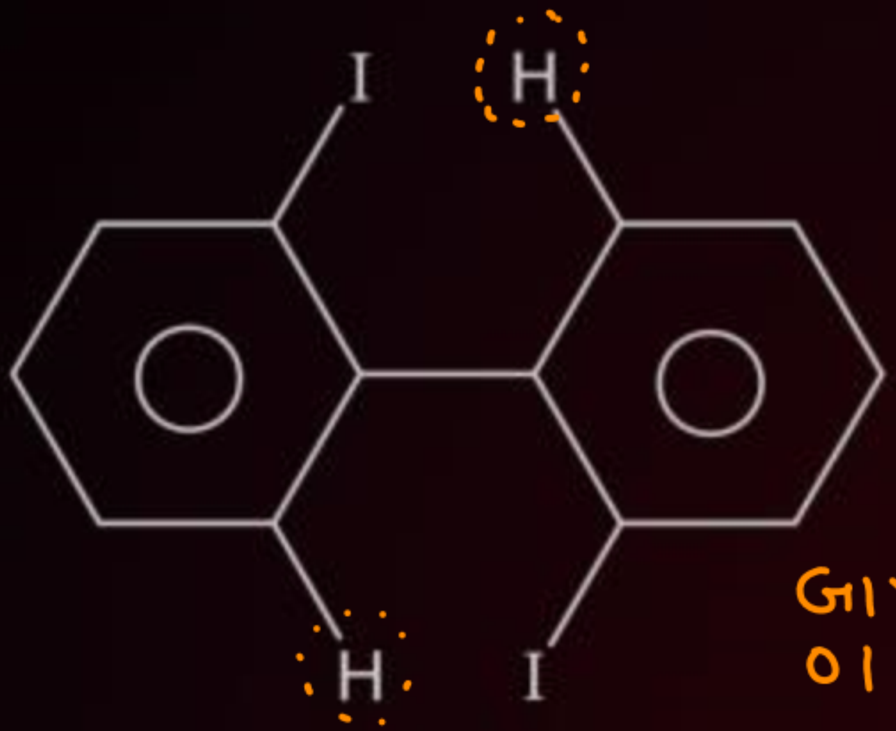
1. 

2. 

3. 

4. 

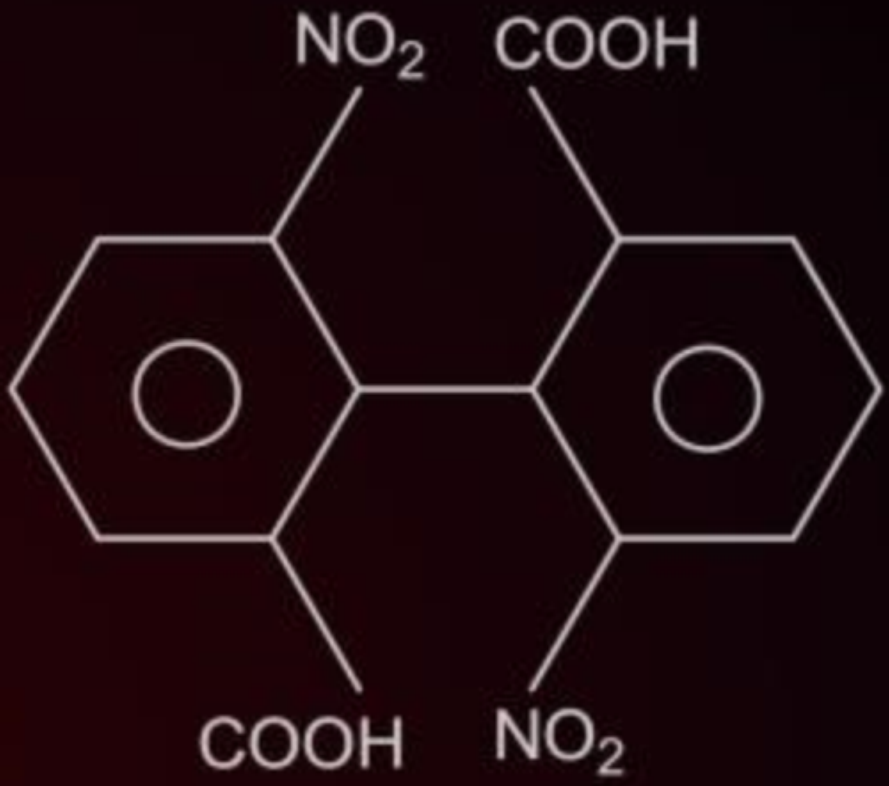
5.



GI ×
OI ×

[redacted]

6.



OI ✓
GI ×

Counting of Isomers

Counting of GI

Unsymmetrical

$TGI = 2^n$

n = GI center

Symmetrical

n = even: $P = \frac{n}{2}$

n = odd: $P = \frac{n+1}{2}$

$TGI = 2^{n-1} + 2^{P-1}$

n = GI center

Counting of OI

Unsymmetrical

Total optically active isomers (A) $= 2^n$

n = OI center

Meso (M) compound $= 0$

Total optical isomer $= A + M$

Enantiomeric pair $= \frac{A}{2}$

Symmetrical

n = even

$P = \frac{n}{2}$

Total optically active isomer (A) $= 2^{n-1}$

(M) Meso $= 2^{P-1}$

Total optical isomer $= (A+M)$

Ena— pair $= \frac{A}{2}$

n = odd

$P = \frac{n+1}{2}$

Total optically active isomer $= 2^{n-1} - 2^{P-1}$

Meso $= 2^{P-1}$

Total optical isomer $= A+M$

Ena— pair $= \frac{A}{2}$

Counting of (GI + OI)

Unsymmetrical

Total Stereoisomer (GI + OI) $= 2^n$

Symmetrical

Total Stereoisomer (GI + OI) $= 2^{n-1} + 2^{P-1}$

$P = \frac{n}{2}$, n = even

$P = \frac{n+1}{2}$, n = odd

(1) $CH_3-\overset{*}{C}H(OH)-\overset{*}{C}H(Br)-\overset{*}{C}H(Cl)-CH_3$

n = 3 | Unsymmetry

optically active $= 2^n = 2^3 = 8$

Meso = 0

Total optical isomer $= A + M = 8$

$EP = \frac{A}{2} = \frac{8}{2} = 4$

(2) $CH_3-\overset{*}{C}H(OH)-\overset{*}{C}H(OH)-CH_3$

n = 2 | Symmetry | $P = \frac{n}{2} = 1$

optically active $= 2^{n-1} = 2$

Meso $= 2^{P-1} = 1$

Total optical Isomer $= A + M = 3$

$EP = \frac{A}{2} = 1$

(3) $CH_3-\overset{*}{C}H(Cl)-\overset{*}{C}H(Br)-\overset{*}{C}H(Cl)-CH_3$ (middle C: → Pseudochiral)

n = 3 | Symmetry | $P = \frac{n+1}{2} = 2$

optically active $= 2^{n-1} - 2^{P-1} = 4 - 2 = 2$

Meso $= 2^{P-1} = 2$

Total optical isomer $= A + M = 4$

EP = 1

(1) $CH_3 - CH \overset{\checkmark}{=} CH - \overset{*}{C}H(CH_3) - CH_2 - CH_3$

$n = 2$

Unsy

Total stereoisomer $= 2^n$
↓
(GI + OI)

$= 2^2$

$= 4$

(2) $CH_3 - \overset{*}{C}H(OH) - \overset{*}{C}H(Br) - CH \overset{\checkmark}{=} CH - CH_3$

$n = 3$

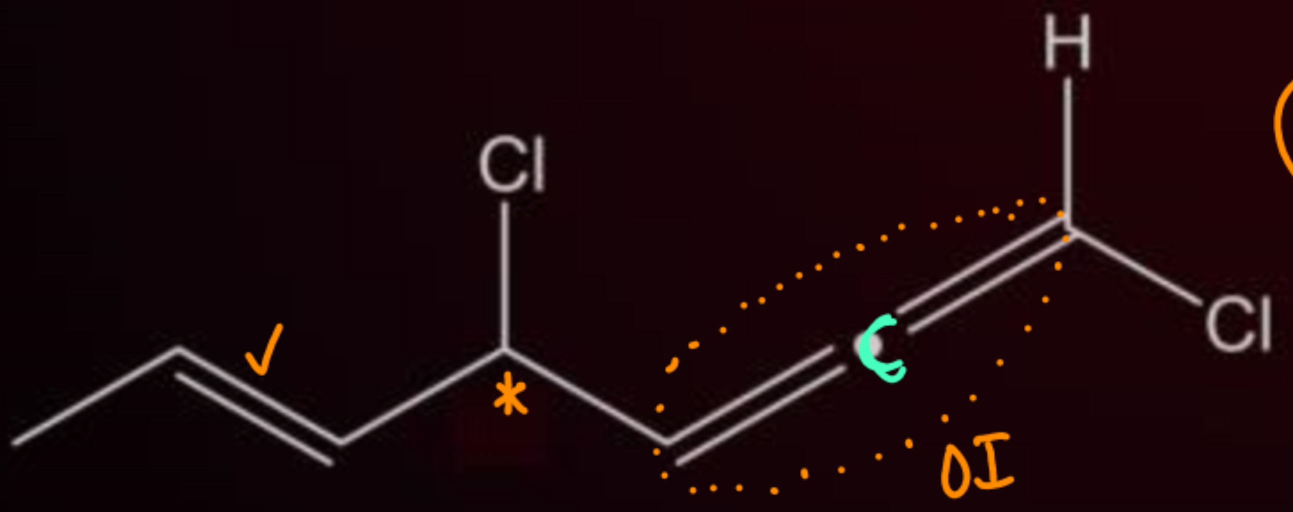
Unsy

Total Stereoisomer $= 2^n$

$= 2^3$

$= 8$

(3)



$n = 3$

Unsy

Total stereoisomer $= 2^n$

$= 2^3$

$= 8$

(4) $CH_3 - \overset{}{C}H = C = C = CH - \overset{*}{C}H(CH_3) - CH_2 - CH_3$

$n = 2$

Unsy

Total Stereoisomer $= 2^n$

$= 2^2$

$= 4$

(5) $CH_3 - \overset{*}{C}H(Cl) - CH = CH - \overset{*}{C}H(Cl) - CH_3$

$n = 3$

Symm

$P = \frac{n+1}{2}$

$P = 2$

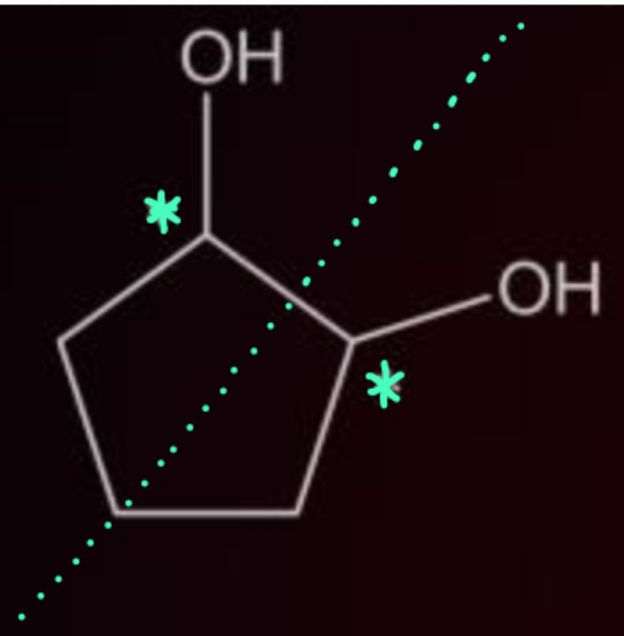
Total Stereoisomer $= 2^{n-1} + 2^{P-1}$

$= 4 + 2$

$= 6$

Note: In cyclic compounds when chiral center and G.I. center are common then count only chiral ~~order~~ for the value of n.

(6)



$n = 2$

Symmetry

$P = \frac{n}{2} = 1$

Total Stereoisomer $= 2^{n-1} + 2^{P-1}$

$= 2 + 1$

$= 3$

(7)



$n = 2$

Symm

$P = \frac{n}{2}$

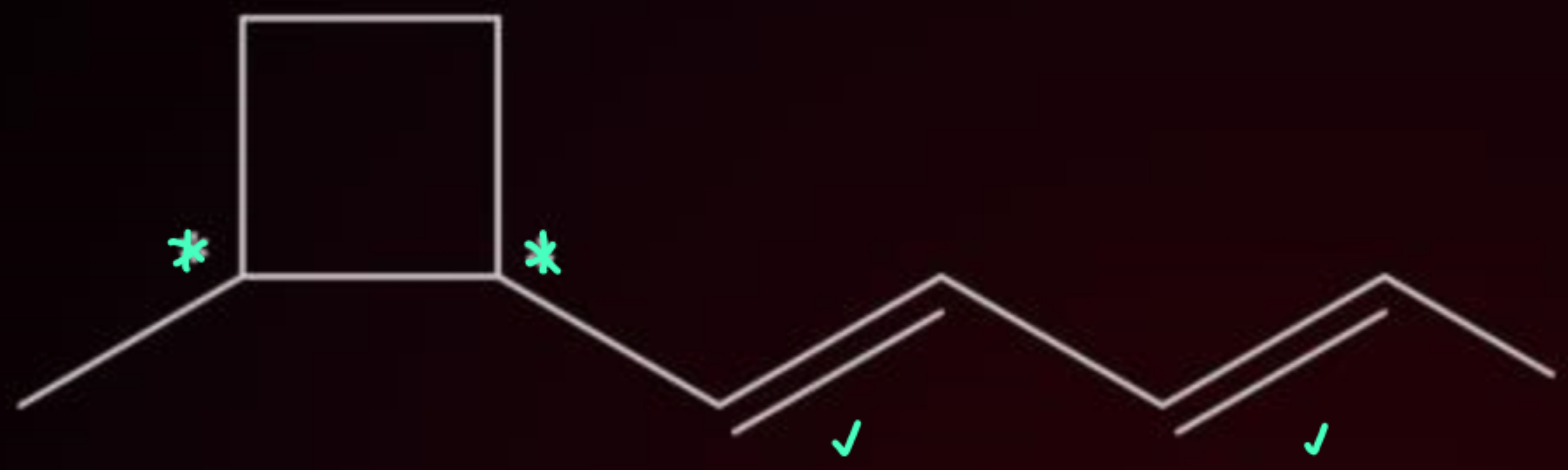
$P = 1$

Total Stereoisomer $= 2^{n-1} + 2^{P-1}$

$= 2 + 1$

$= 3$

(8)



$n = 4$

Unsymmetry

$n = 4$

$$\text{Tstereoisomer} = 2^n = 2^4 = 16$$

Dipole Moment

→ denoted by (μ)
→ unit → debye

→ Comp is polar or nonpolar. ($\mu = 0$ nonpolar; $\mu \neq 0$ polar)

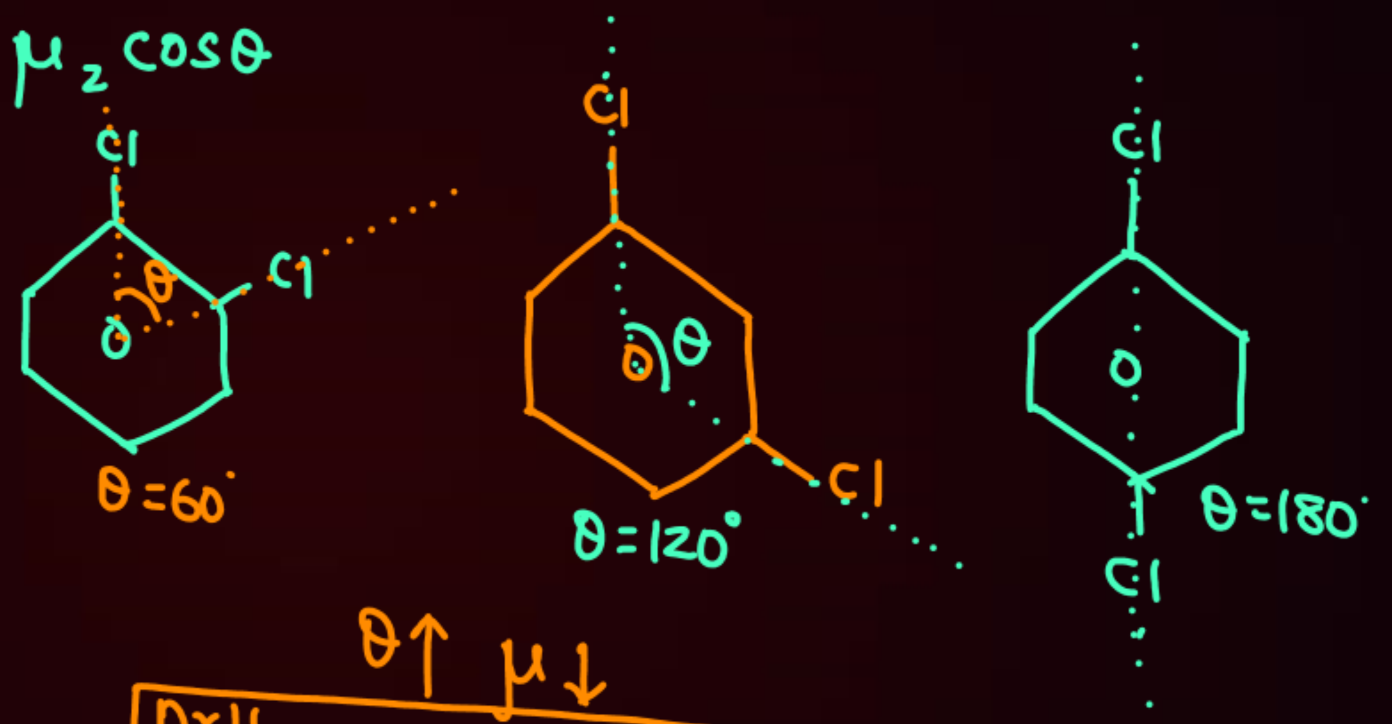
→ vector quantity.

→ $|\vec{\mu}| = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$

→ $\theta \uparrow$ $\cos\theta \downarrow$ $\mu \downarrow$

→ draw arrow from less EN to more EN

→ Equal & opposite vector cancel out eachother
$\mu = 0$ (nonpolar)

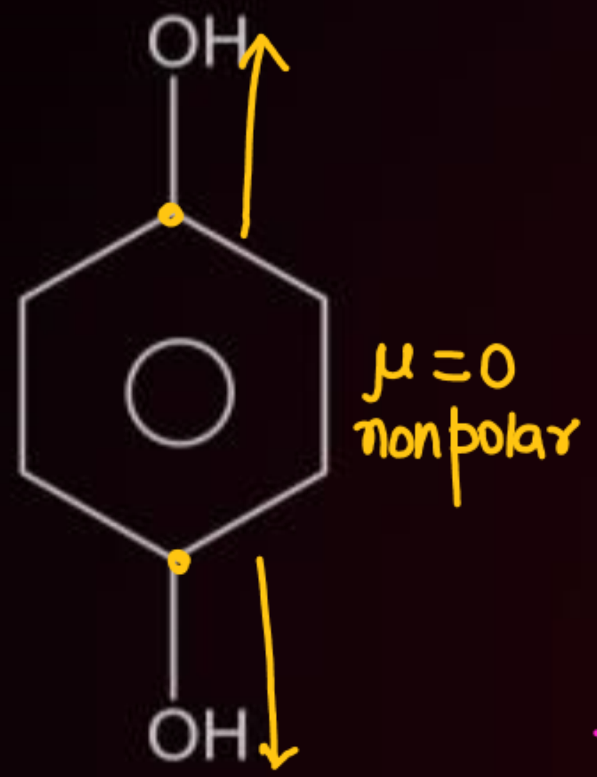


$\theta \uparrow$ $\mu \downarrow$

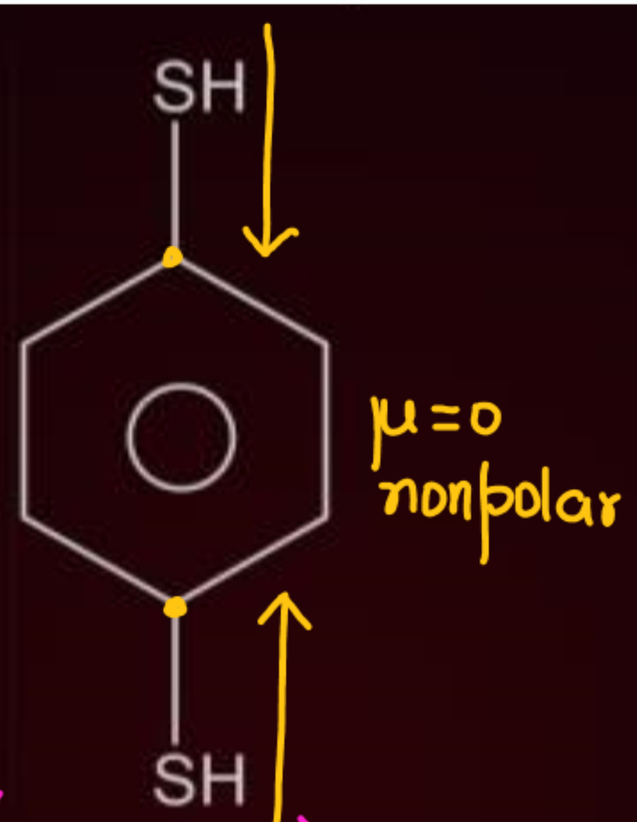
Ortho > meta > para

Que. Which of the following has non-zero dipole moment?

1.

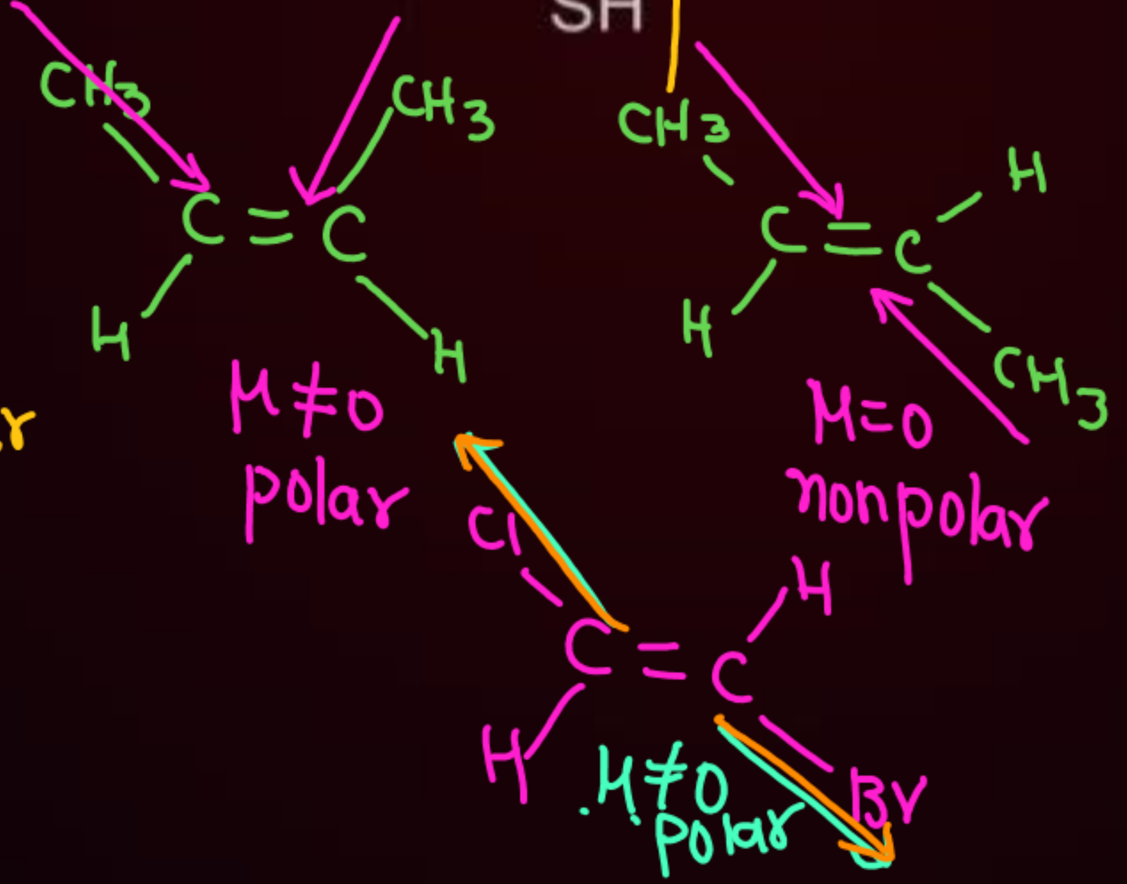


2.

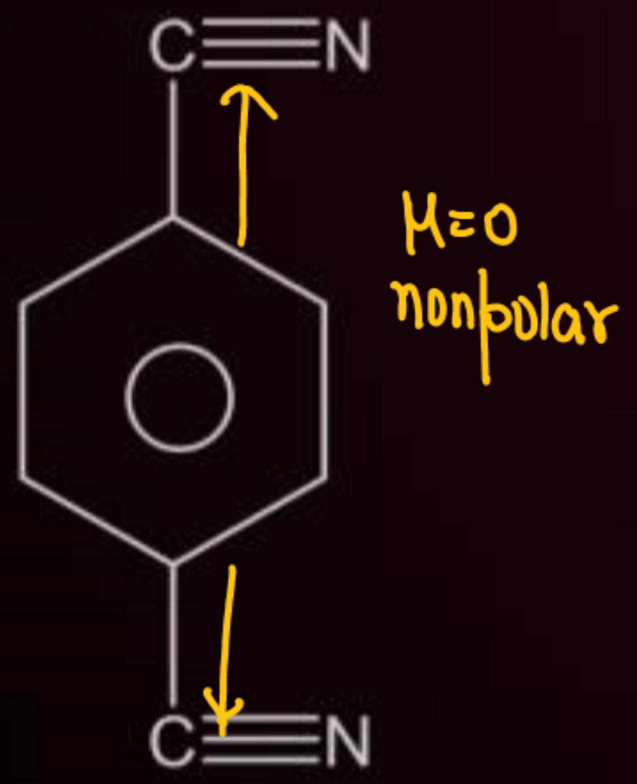


3.

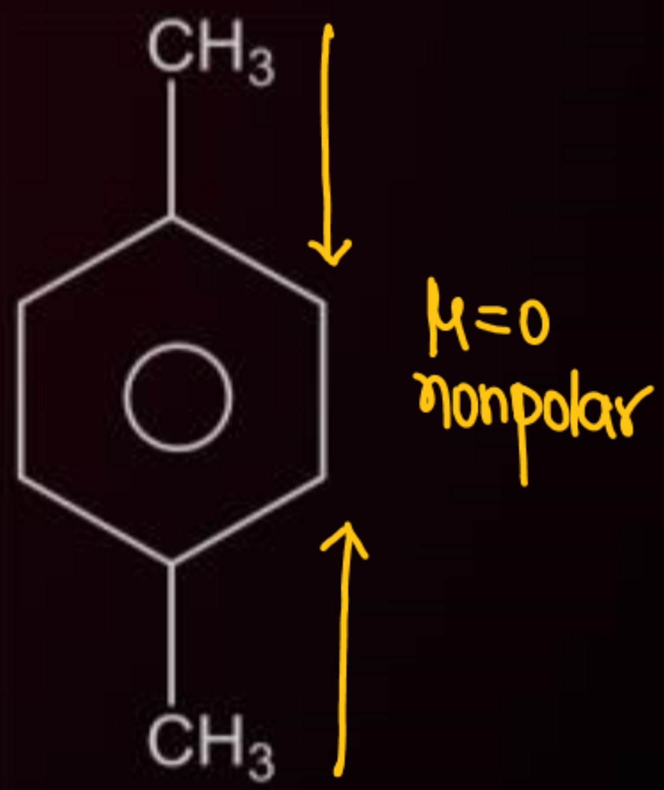




4.



5.



(5) Boiling point (B.P.)

① B.P. $\propto$ Polarity $\propto$ Dipole moment (μ)

② B.P. $\propto$ Mol. wt.

B.P. $\propto$ Surface area

} Vander wall force of attraction ↑

③ B.P. $\propto \frac{1}{\text{Branching}}$ [If mol. mass same]

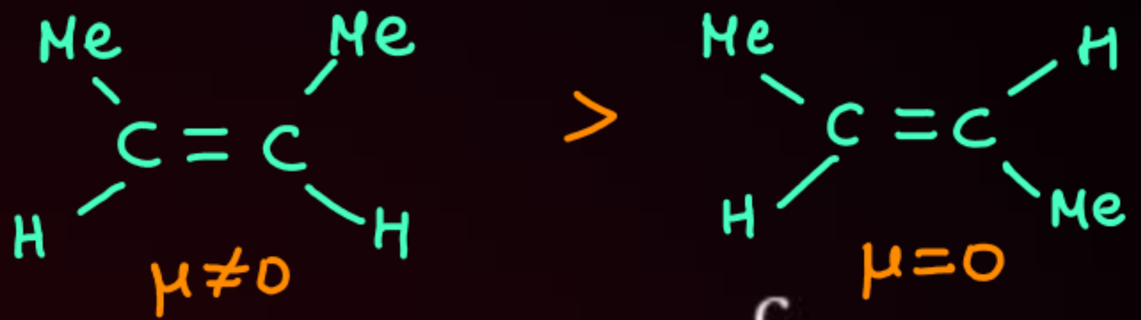
④ B.P. $\propto$ Intermolecular force of attraction

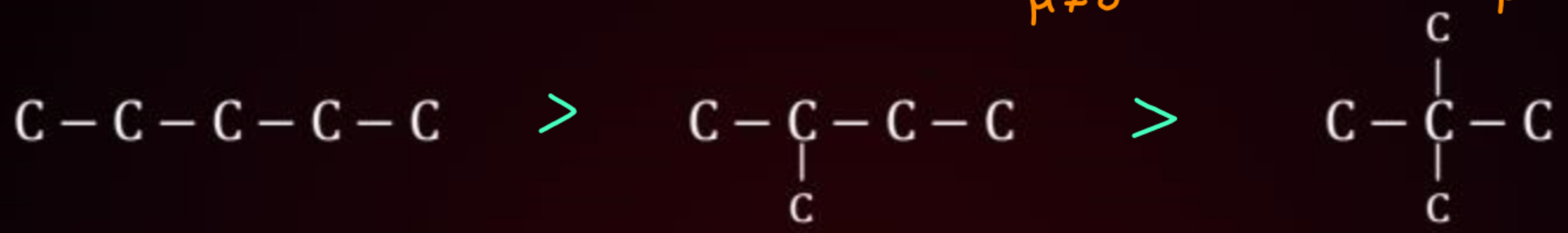
- → H-bonding
- → Dipole-dipole attraction

Compare BP

Ex.- C_5H_{12}

$BP \propto \frac{1}{\text{branch}}$





Ex.-

$CH_2 - OH$
|
$CH_2 - OH$

Ethylene glycol
(Glycol)

<

$CH_2 - OH$
|
$CH - OH$
|
CH_2OH

Glycorol/Glycerine
(More H-bond)

(Boiling point)

(6) Melting point:

① M.P. ∝ Mol. wt.

② M.P. ∝ Symmetry of molecules (Packing efficiency)

If Void ↑ ⟹ M.P. ↓



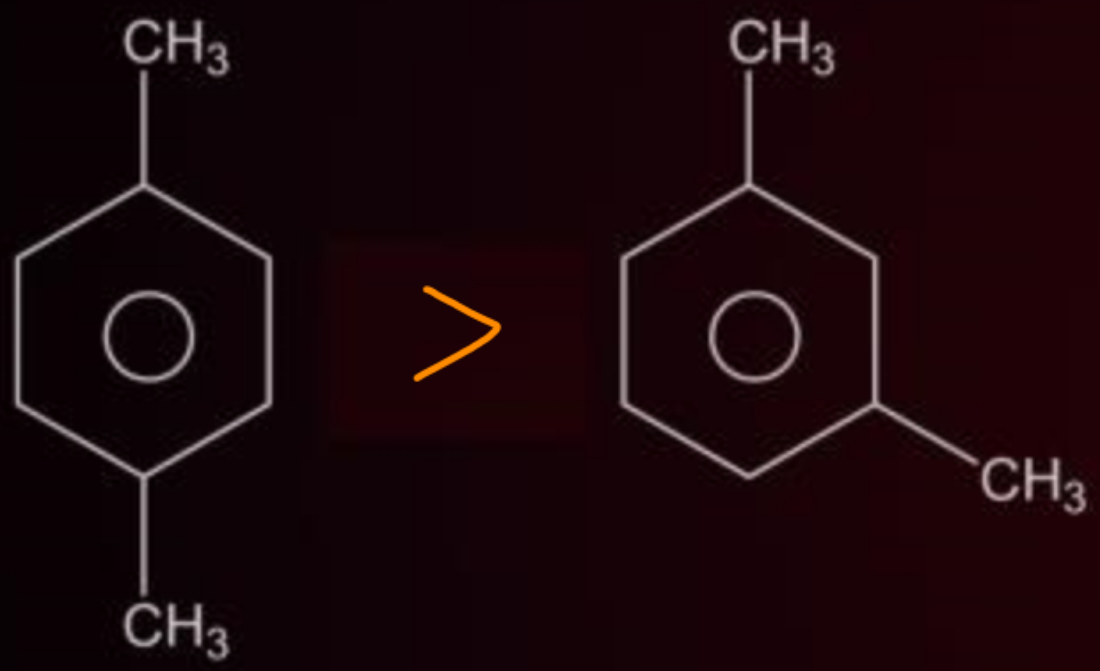
Trans (packing ↑)



Cys packing ↓

MP → Trans > cys

Ex.- M.P



Solubility ∝ μ

Ex.-

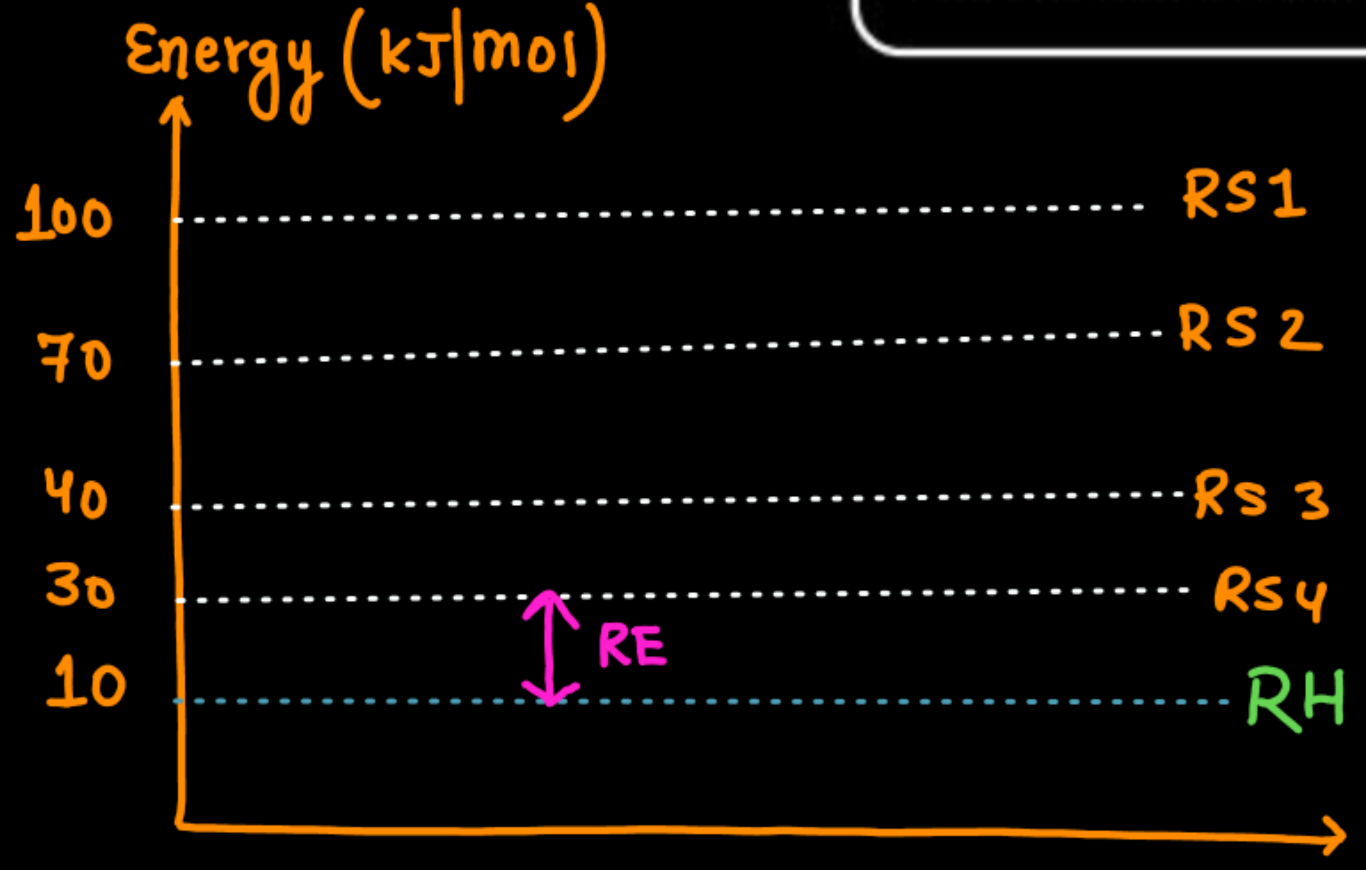
				
(I)	μ	cys	>	Trans
(II)	B.P	cys	>	Trans
(III)	M.P	cys	<	Trans
(IV)	Stability	cys	<	Trans

THANK YOU
All the Best!!

It is k/a Stabilisation Energy.

Resonance Energy

(Based on HOH)



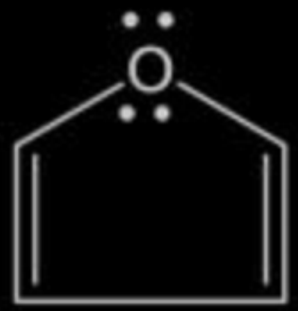
Resonance Energy = (30 − 10) kJ/mol
= 20 kJ/mol

1. Most Stable Resonating Str = RS 4
2. Resonance Hybrid → Most Stable & least Energy
3. Resonance Energy → Energy gap b/w most stable Resonating str & Resonance Hybrid is called Resonance energy.
4. Experimentally Resonance Energy = Theoretical HOH − Experimental HOH

* More Resonance ⇒ More Resonance Energy released.
* More stable more RE released.
* If new charge is developed due to Resonance then Resonance Energy ↓.

Examples:

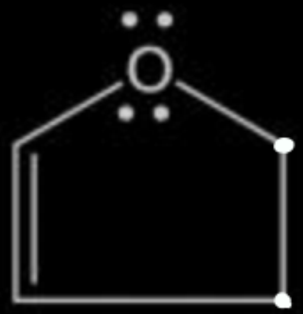
1.



(A)



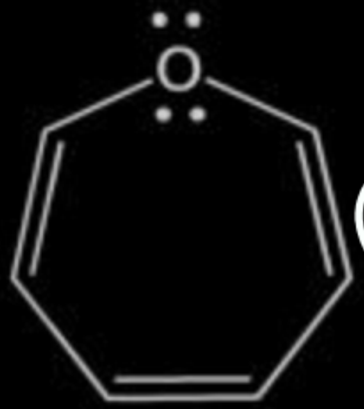
(AA)



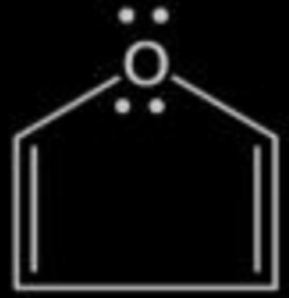
(NA)

a > c > b

2.



(NA)



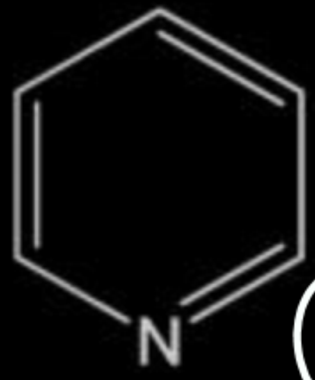
(A)



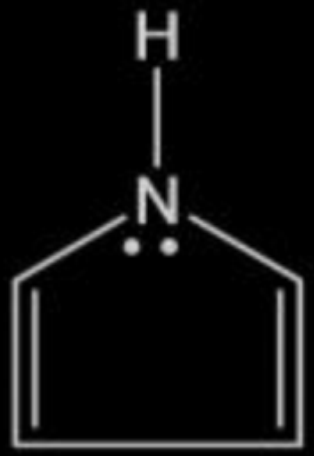
(AA)

b>a>c

3.



(A) more Reso



(A)

a>b

4.



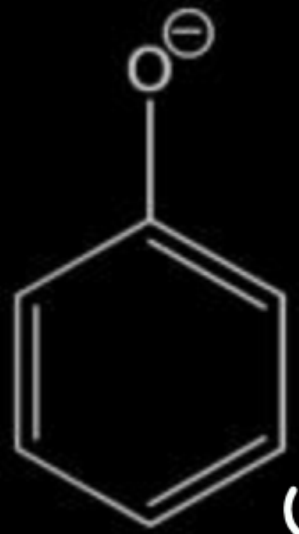
(A)



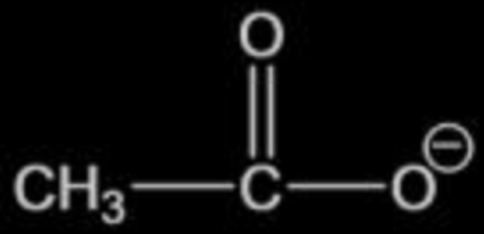
(A)

b>a

5.



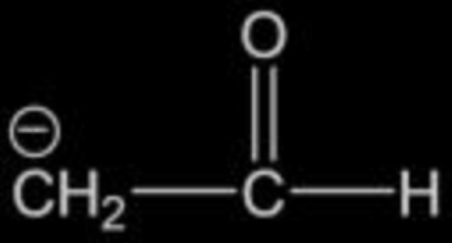
Reso
(normal)



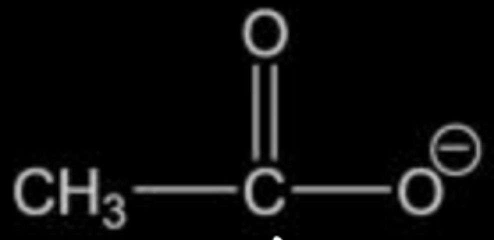
Reso
(Eq + Reso)

b>a

6.

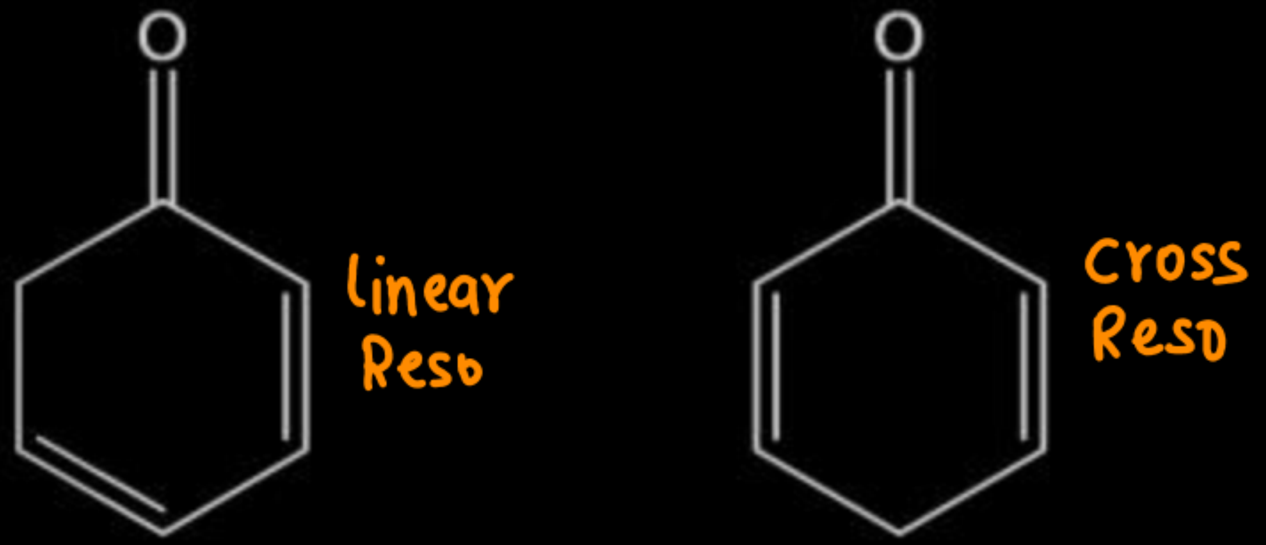


normal
Reso

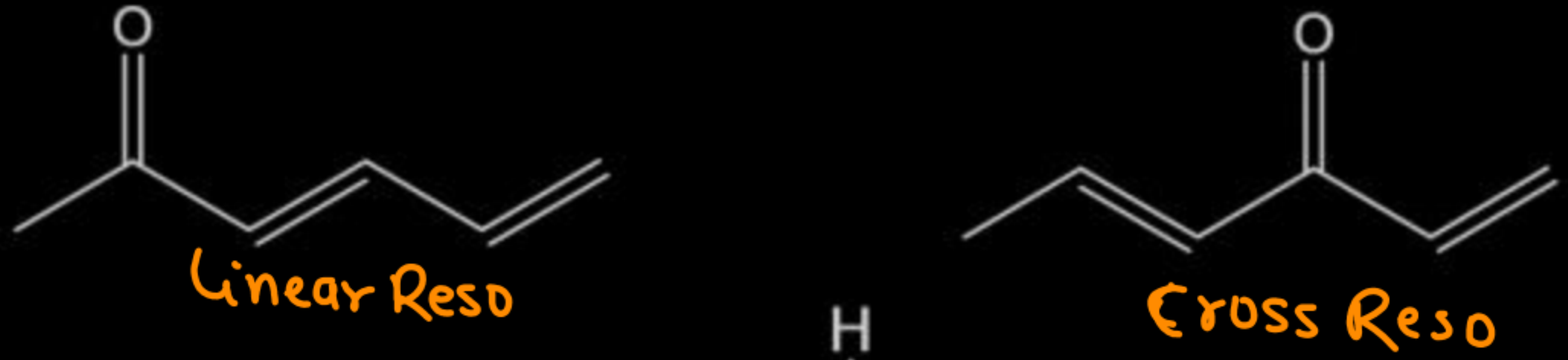


Eq+ Reso

b>a

7. 

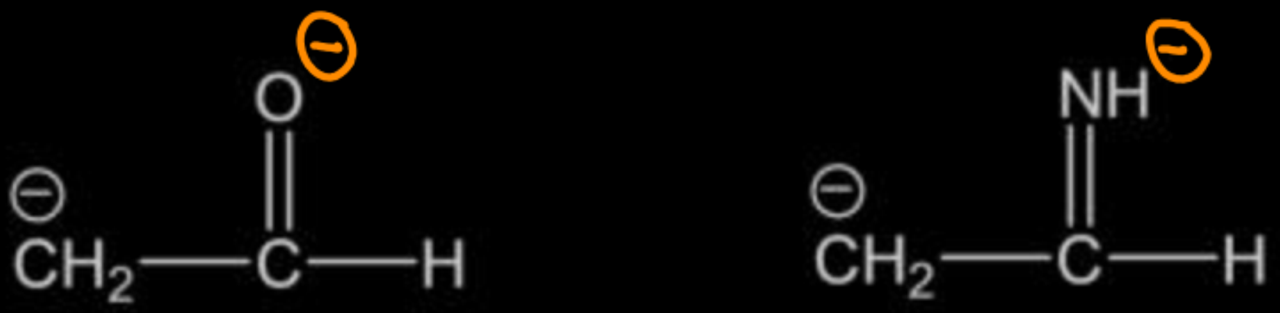
a>b

8. 

a>b

9. 

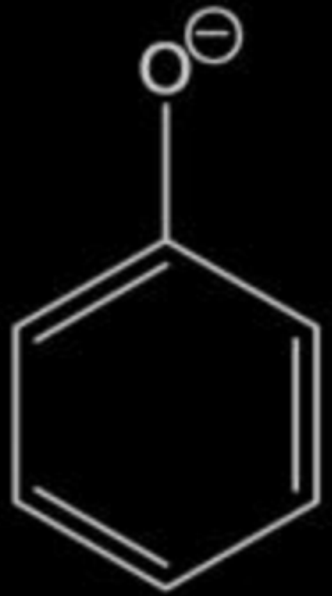
b>a

10. 

a>b

11.





b>a

new charge develop

12. $CH_2{=}CH{-}OH$ $\quad$ $CH_2{=}CH{-}O^{\ominus}$ $\quad$ b>a

new charge develop

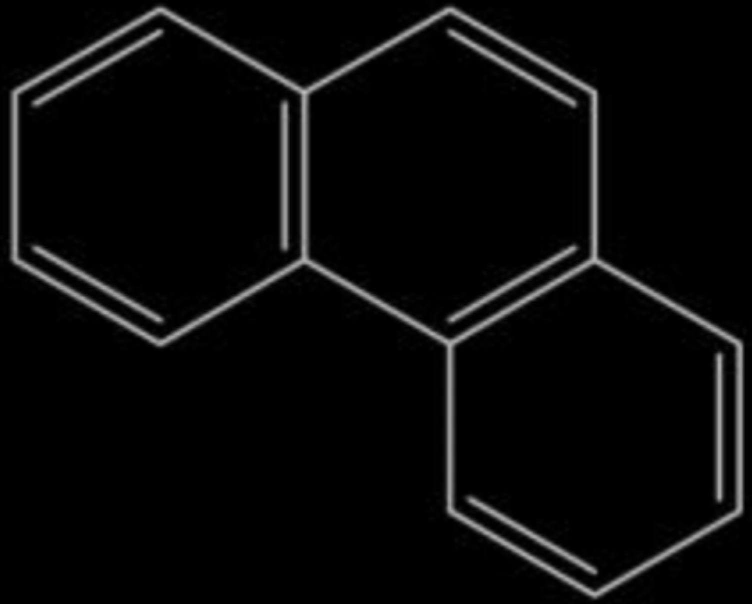
13. $CH_2{=}CH{-}\ddot{N}H_2$ $\quad$ $CH_2{=}CH{-}\ddot{O}H$ $\quad$ a>b

good Reso

14.

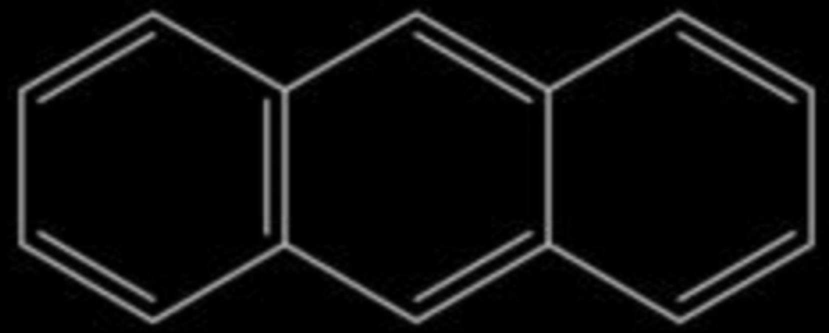






c>b>a

15.





b>a

more Reso

more stability

more Stabilisation Energy

Bond Parameter

1. Bond order
2. Bond Length

Bondorder

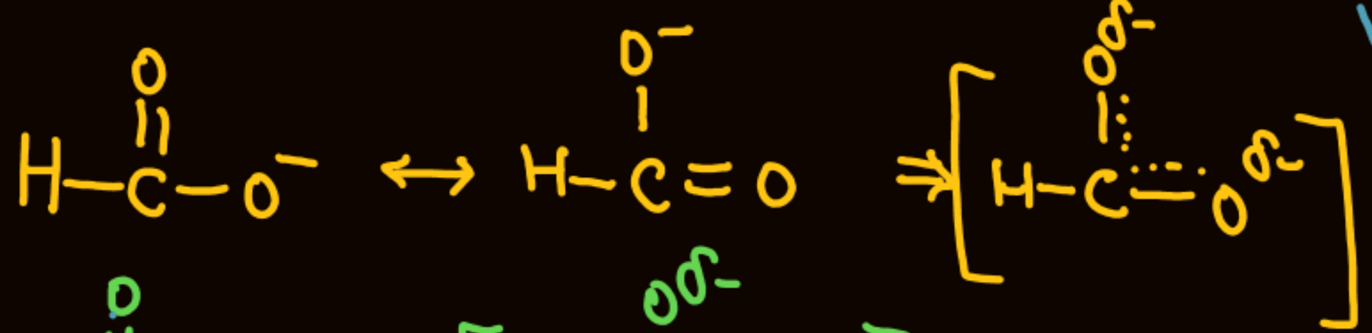
Contribution of bond in a molecule is called Bondorder.

CH_3-CH_3 BO = 1

$CH_2=CH_2$ BO = 2

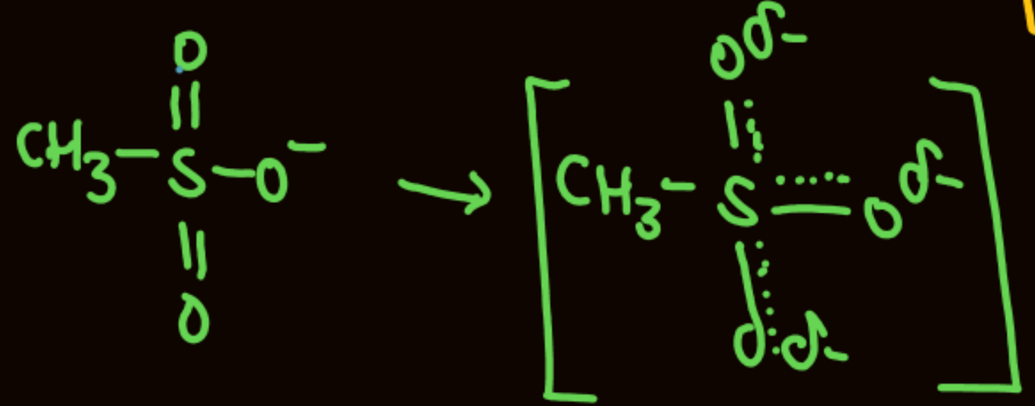
$CH\equiv CH$ BO = 3

Bond order of Resonace Str



VTS $BO = \frac{\sigma + \pi}{\sigma}$

$BO = \frac{2+1}{2} = \frac{3}{2} = 1.5$



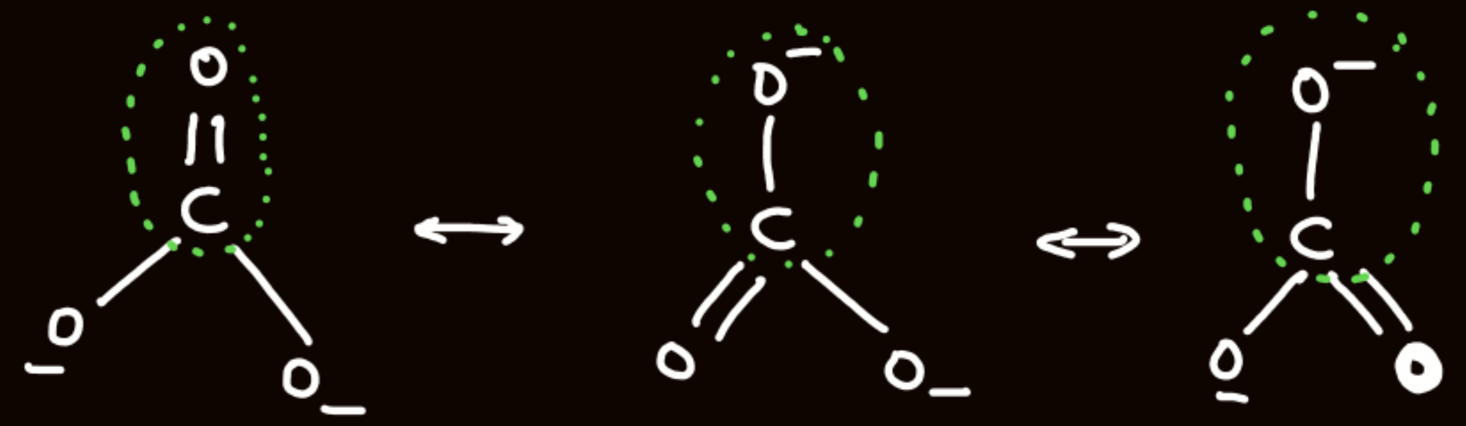
$BO = \frac{\sigma + \pi}{\sigma} = \frac{3+2}{3} = \frac{5}{3} = 1.66$

Bond order (Resonance) = $\frac{\text{Total num of bond b/w specific atom}}{\text{Total num of Resonating str}}$

VTS

$BO = \frac{\sigma + \pi}{\sigma}$

Eg



Bond order = $\frac{4}{3}$ = 1.33

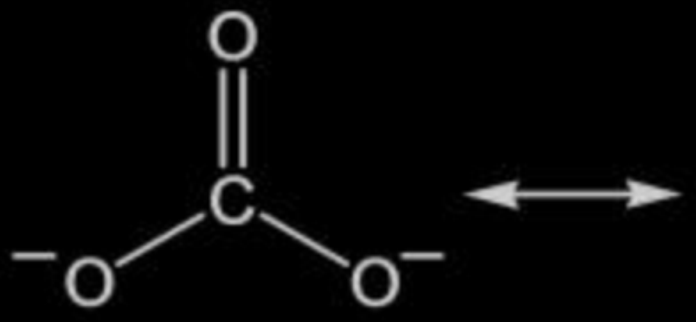
$BO = \frac{3+1}{3}$

$= \frac{4}{3}$

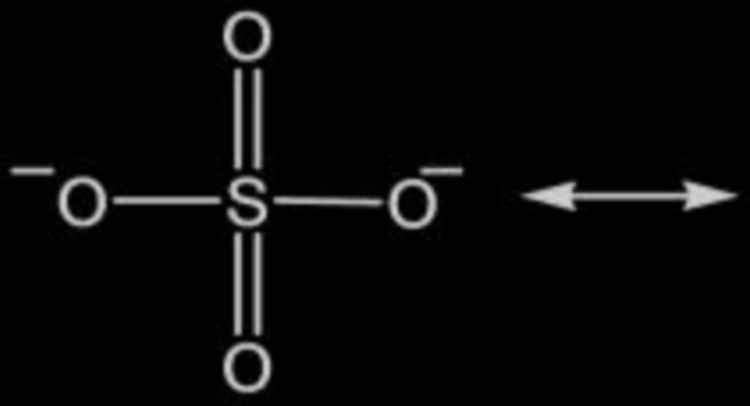
$= 1.33$

संबंध

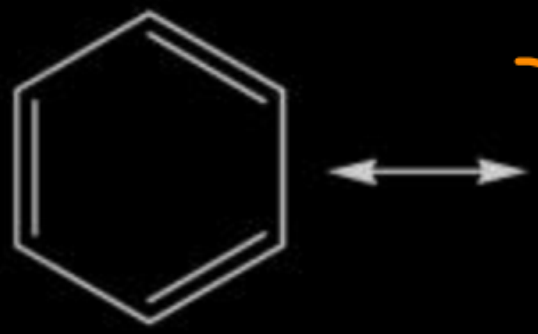
Bondorder ∝ π bond ↑ ∝ Bond strength ∝ Bond Energy ∝ Bond Stability ∝ $\frac{1}{\text{Bond length}}$

1. 

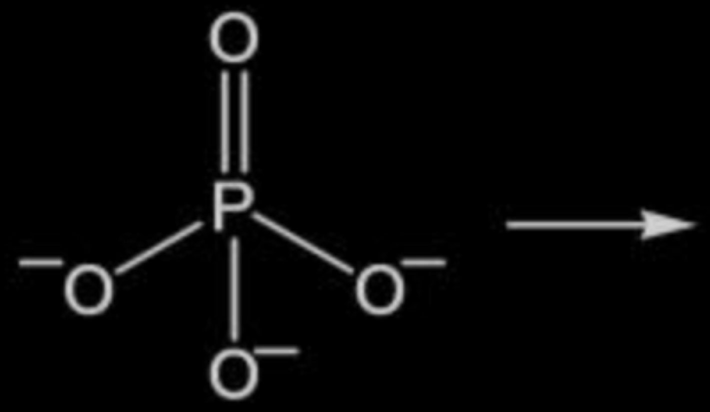
$$\frac{\sigma+\pi}{\sigma} = \frac{3+1}{3} = 1.33$$

2. 

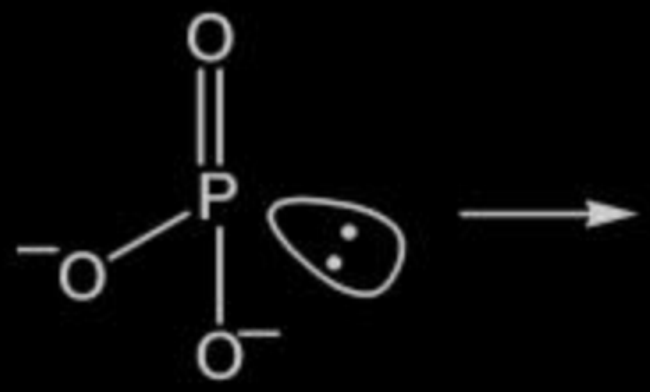
$$\frac{\sigma+\pi}{\sigma} = \frac{4+2}{4} = \frac{6}{4} = 1.5$$

3. 

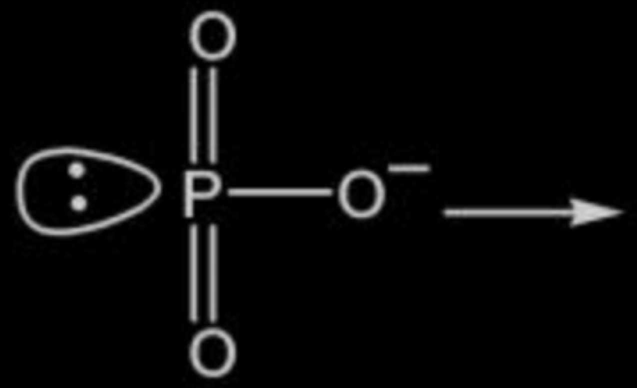
$$\frac{\sigma+\pi}{\sigma} = \frac{6+3}{6} = \frac{9}{6} = 1.5$$

4. 

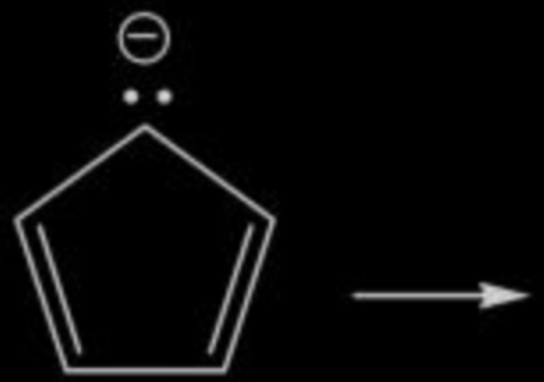
$$\frac{\sigma+\pi}{\sigma} = \frac{4+1}{4} = \frac{5}{4} = 1.25$$

5. 

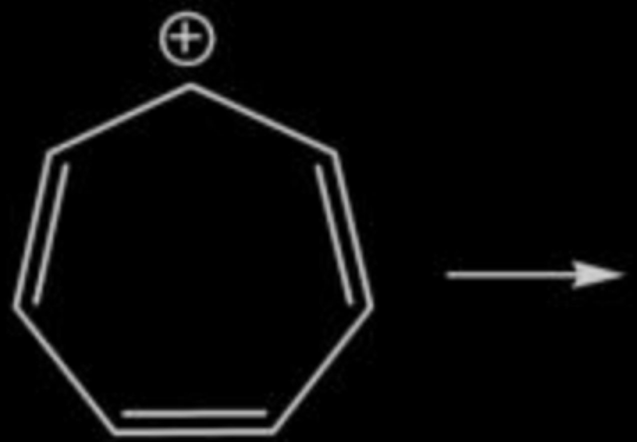
$$\frac{\sigma+\pi}{\sigma} = \frac{3+1}{3} = \frac{4}{3} = 1.33$$

6. 

$$\frac{\sigma+\pi}{\sigma} = \frac{3+2}{3} = \frac{5}{3} = 1.66$$

7. 

$$\frac{\sigma+\pi}{\sigma} = \frac{5+2}{5} = \frac{7}{5} = 1.4$$

8. 

$$\frac{\sigma+\pi}{\sigma} = \frac{7+3}{7} = \frac{10}{7} = 1.42$$

9. 

$$\frac{\sigma+\pi}{\sigma} = \frac{3+1}{3} = \frac{4}{3} = 1.33$$

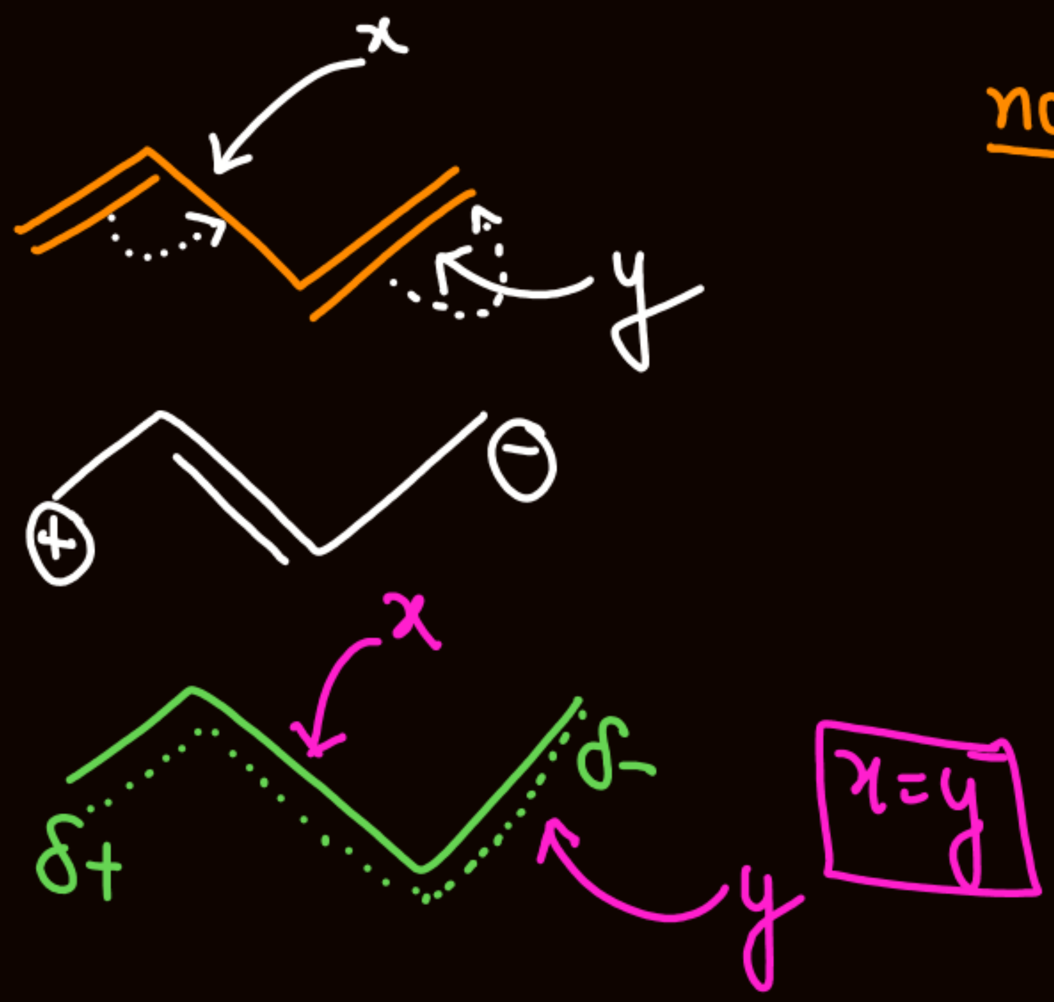
Bond Length

H_3C-CH_3	Bond length	1.54 Å
$H_2C=CH_2$	Bond length	1.34 Å
$HC\equiv CH$	Bond length	1.20 Å

Bond length → Single bond > Double bond > Triple bond

Single bond > partial double bond > Complete double bond > partial triple bond > complete triple bond

Eg



note → Due to Resonance → Single bond → partial double bond

Bond length ↓

Due to Resonance Single bond छोटा हो जाता है।

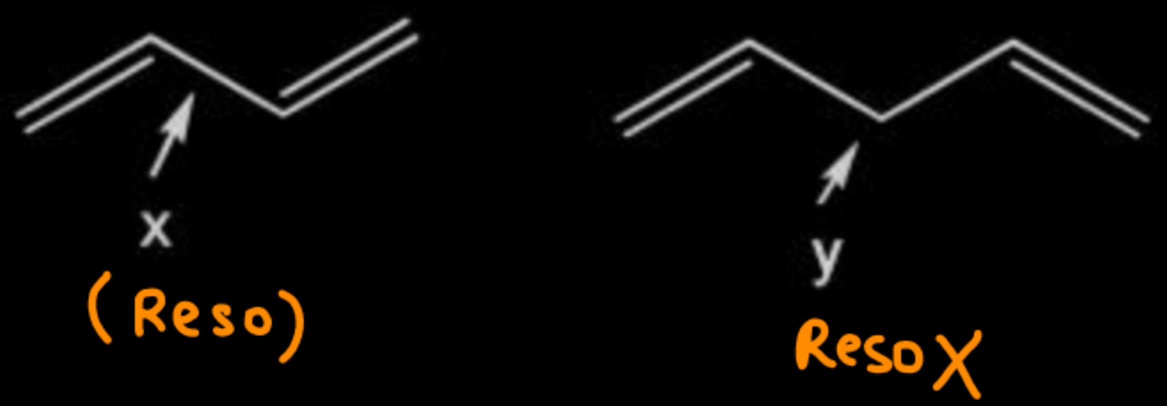
Due to Resonance → double bond → partial double bond

Bond length ↑

Due to Resonance double bond बड़ा हो जाता है।

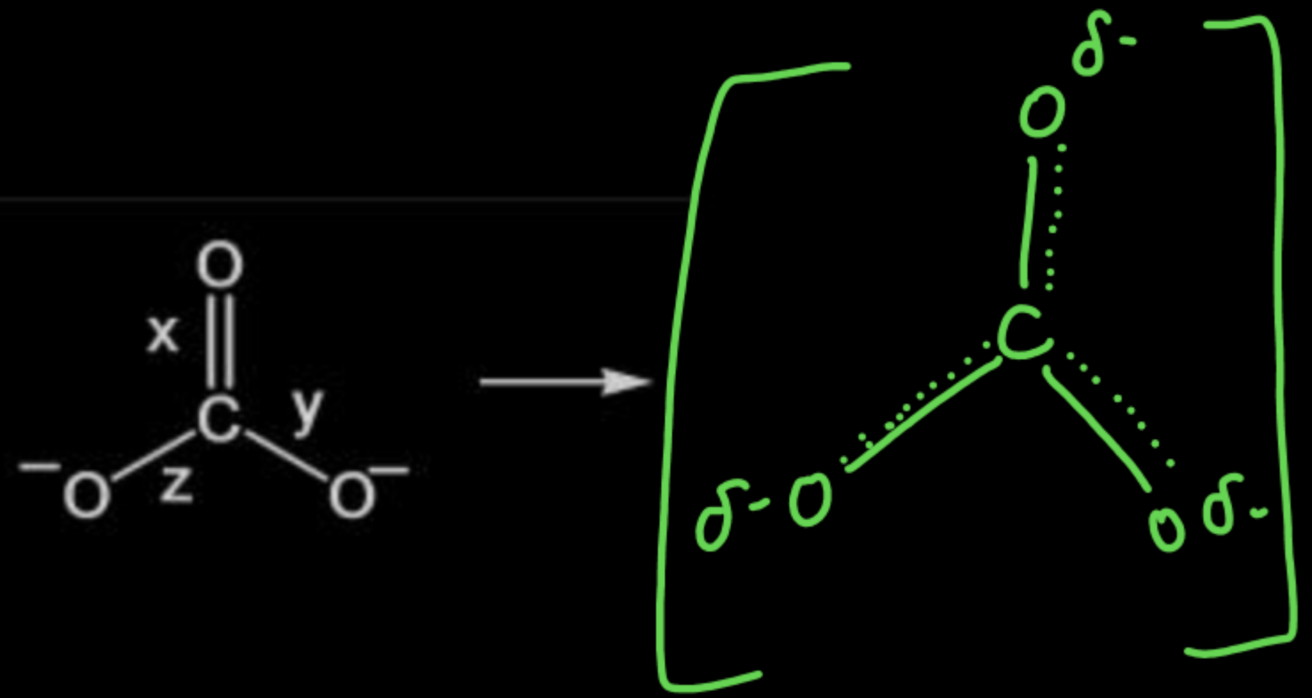
Bond Lenghth

11.

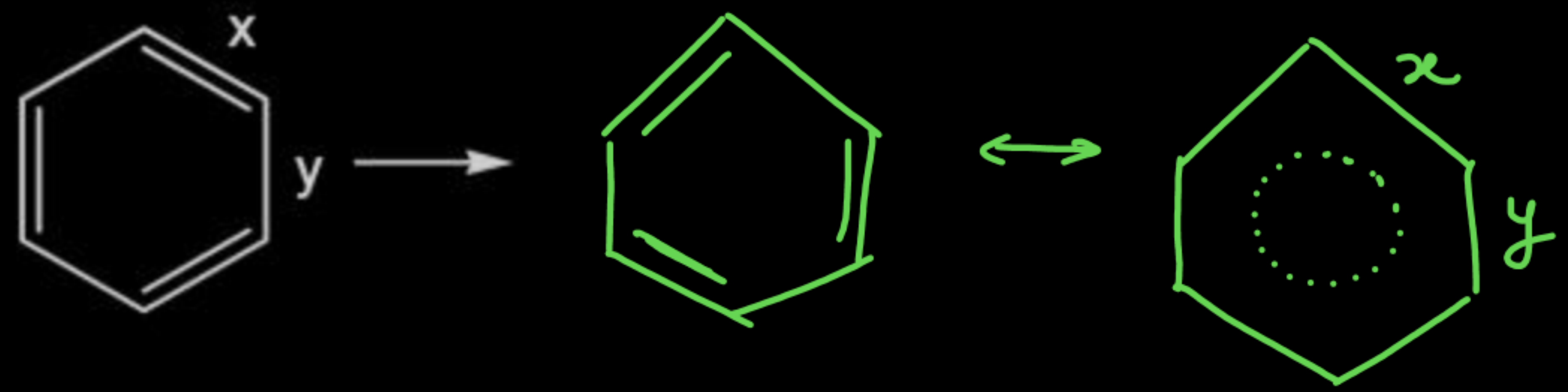


$x < y$

12.



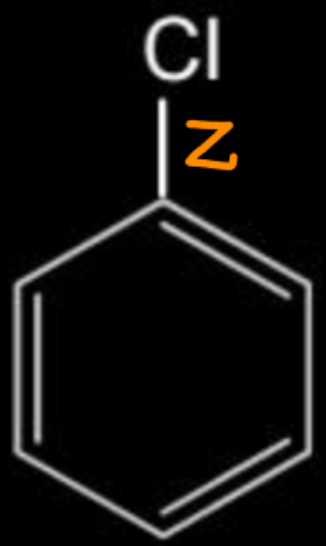
$x = y = z$

13. 

$x = y$

14. $CH_2{=}CH\underset{x}{—}\ddot{C}l:$ Reso ✓

$CH_3\text{-}CH_2\text{-}CH_2\underset{y}{—}Cl$ Reso ✗



Reso ✓

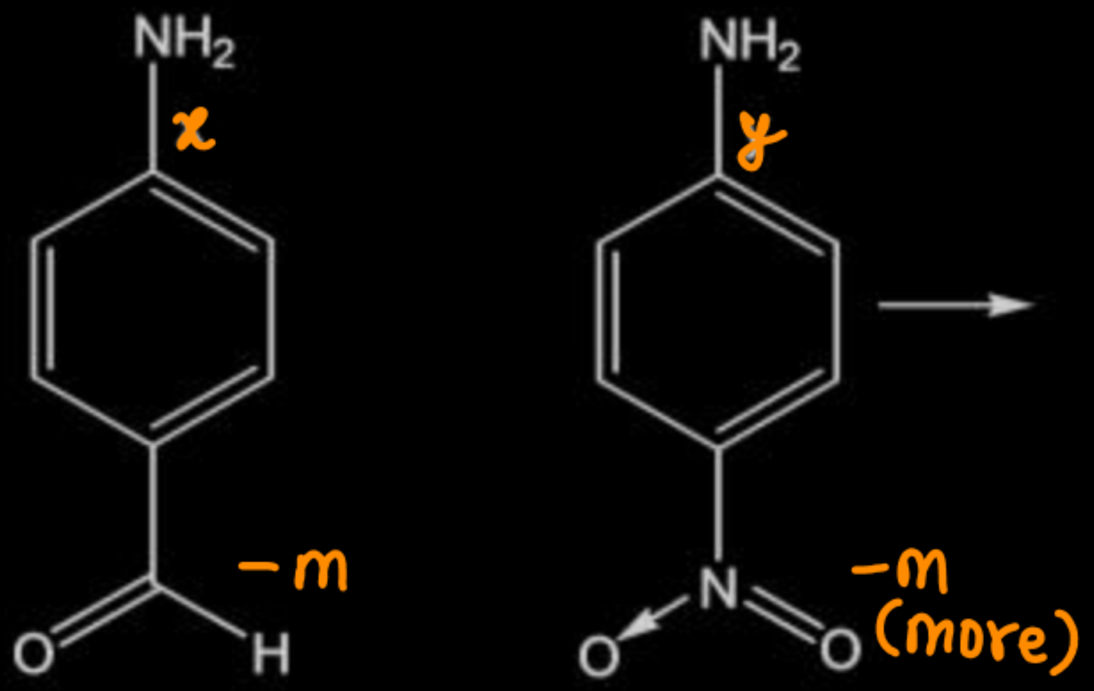
$y > x > z$

15. $CH_2{=}CH\underset{x}{—}\ddot{O}Me$

$CH_2{=}CH_2\underset{y}{—}\ddot{N}H_2$ less En (more Reso)

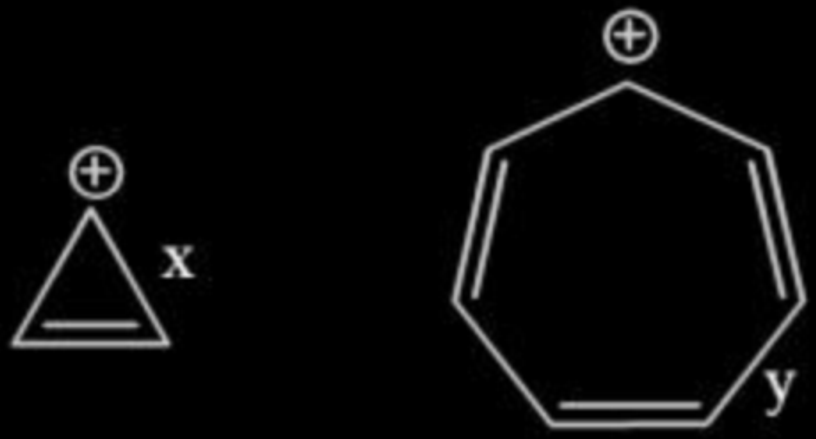
$x > y$

16.



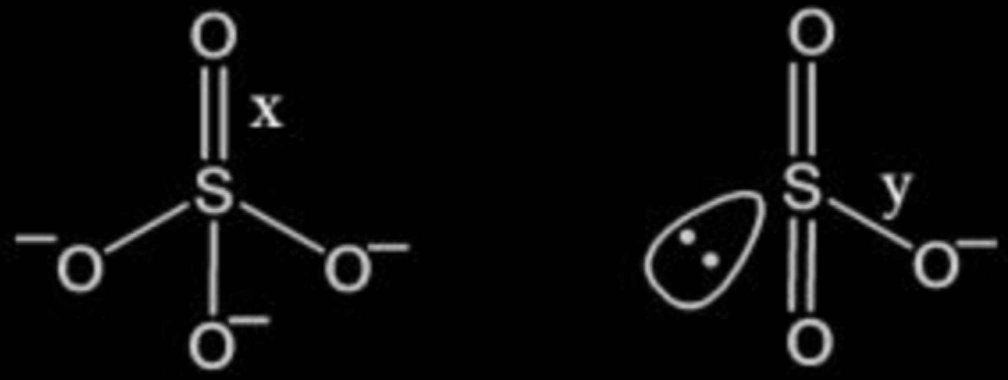
Bondlength → $x > y$

17.

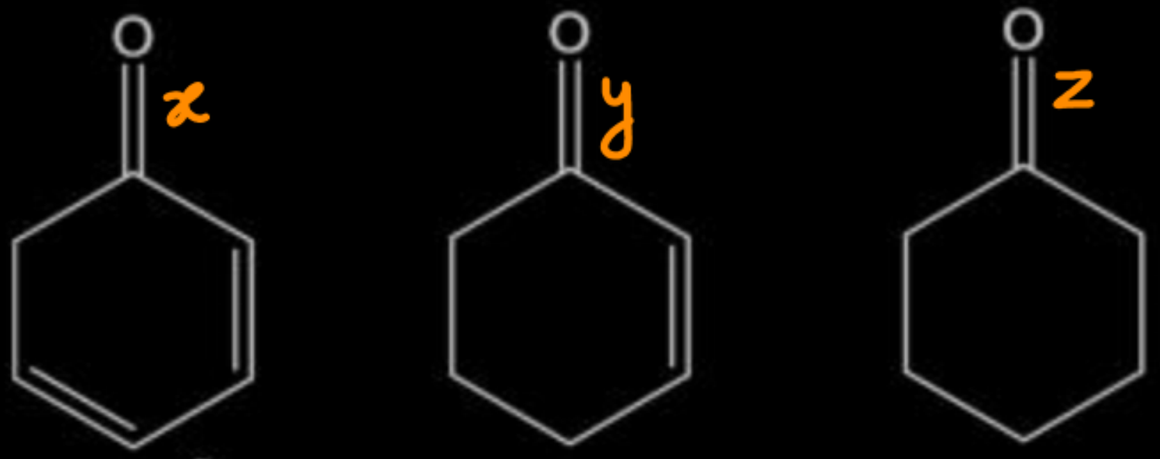


$x > y$

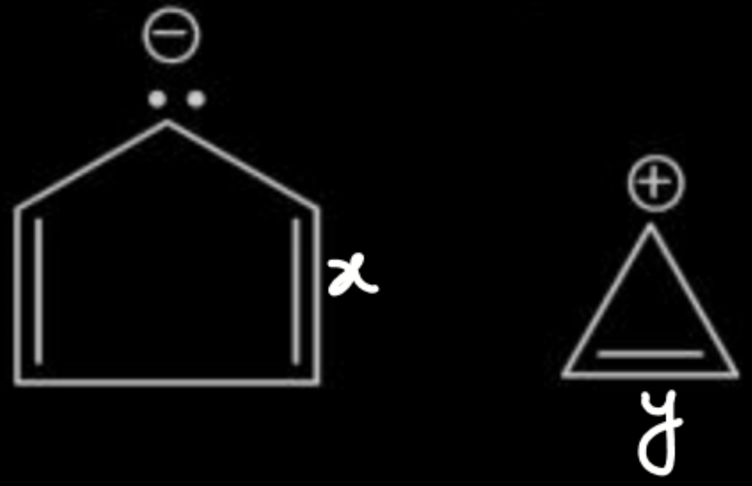
18.



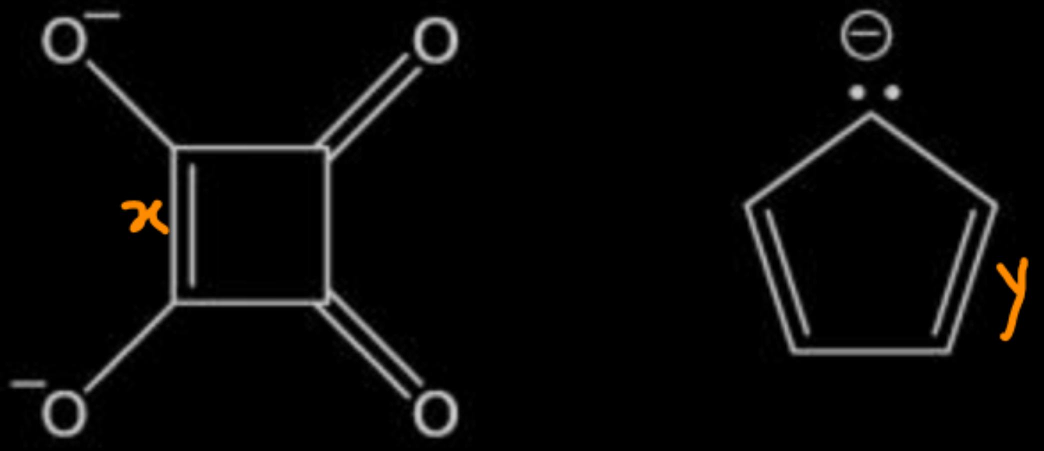
$x < y$

22. 

x > y > z

23. 

x > y

24. 

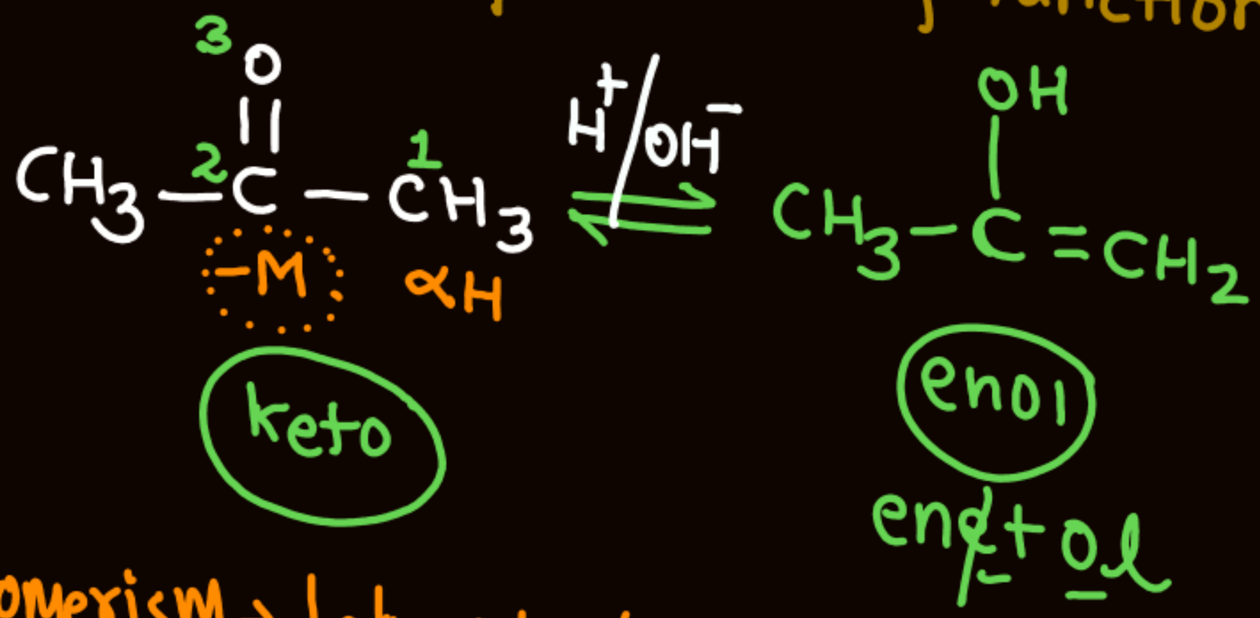
x > y

25. $CH_2{=}CH{-}CH{=}CH{-}O^{\ominus}$ (x) $CH_2{=}CH{-}O^{\ominus}$ (y)

y > x

Tautomerism

* Str isomerism which exists in dynamic equilibrium is Called Tautomerism.
* Transfer of H^+ / Delocalisation of H^+ / Movement of H^+ in a molecule is Tautomerism.
* also k/a cationotropy ((+) movement) / protonotropy (H^+ movement) / Desmotropy (charge transfer).
* Found in acidic as well as basic medium.
* position of C—H sigma bond changes (position of H atom changes)
* Tautomerism is a special case of functional isomerism.



(ketoenol tautomerism)
↓
VTS

{ 2, 3 का bond 1, 2 में
1 का Hydrogen 3 में
transfer करना है। }

Tautomerism → Intramolecular transfer of H^+
→ Transfer of αH / acidic H / active H

Condition of Tautomerism

① −M Group must be present.

② atleast 1 αH must be present. (either directly connected or after resonance)

H−C(=O)−H ✗

$H_2\ddot{N}-C(=NH)-\ddot{N}H_2$ ✓

$H-C(=O)-CH_3$ ✓

$CH_3-NO_2 \rightarrow CH_3-N(=O)\rightarrow O$ ✓

$CH_3-C(=O)-CH_3$ ✓

$H-C(=O)-NH_2$ ✓

$CH_3-NO \rightarrow CH_3-N=O$ ✓

$NH_2-C(=O)-NH_2$ ✓

$H_3C-C(=O)-NH_2$ ✓

$CH_3-CN \rightarrow CH_3-C\equiv N$ ✓

$H-C(=NH)-CH_3$ ✓

$H_2N-C(=NH)-CH_3$ ✓

$CH_3-CH=CH-C(=O)-H$ ✓

$CH_3-\overset{+}{C}H_2$ ✗

$CH_3-CH_2^-$ ✗

$CH_3-\ddot{N}H_2$ ✗

$CH_3-C(CH_3)_2-C(=O)-H$ ✗



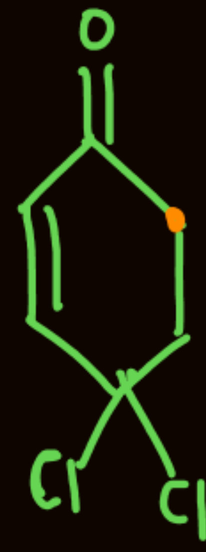
✓



✓



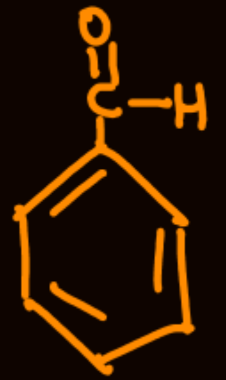
✗

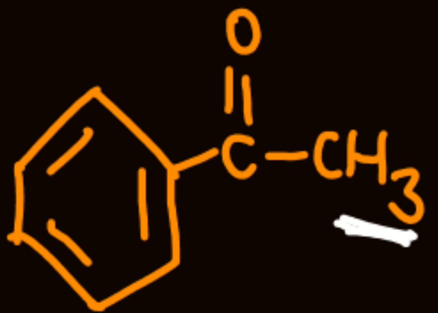


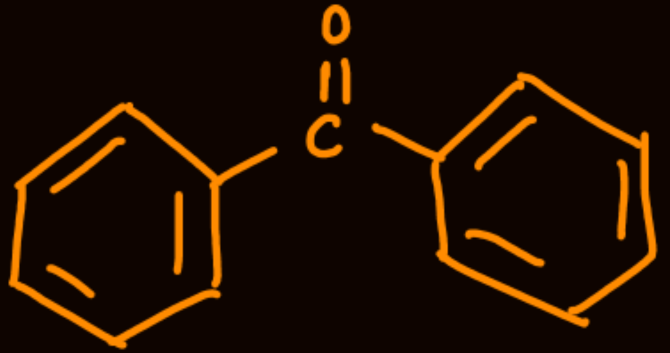
✓

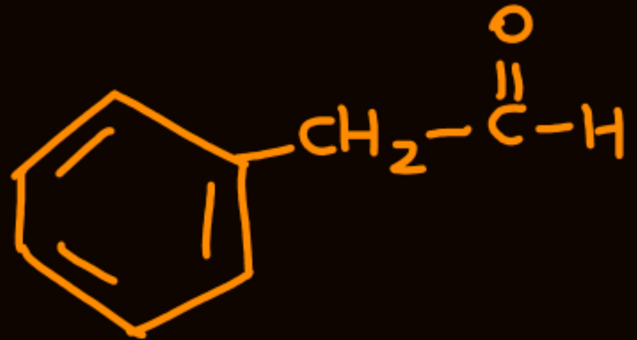


 ✗

 ✗

 ✓

 ✗

 ✓

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (a, b, c)

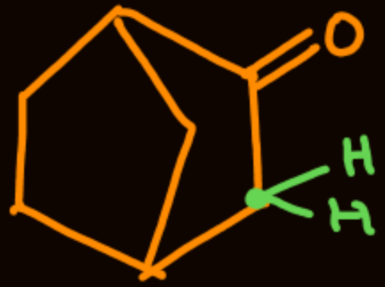
b → Tautomerism (more)

b → active methylene group

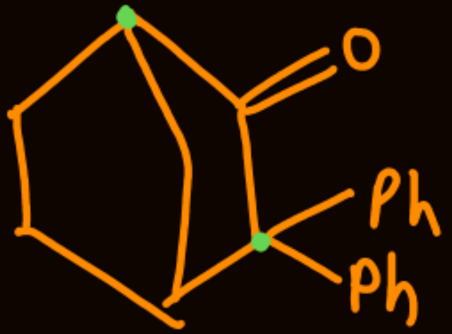
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$ (a, b)

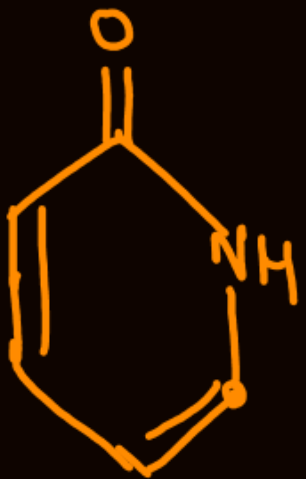
b → Tautomerism (more)

 ✓

 ✓

 ✗

 ✗

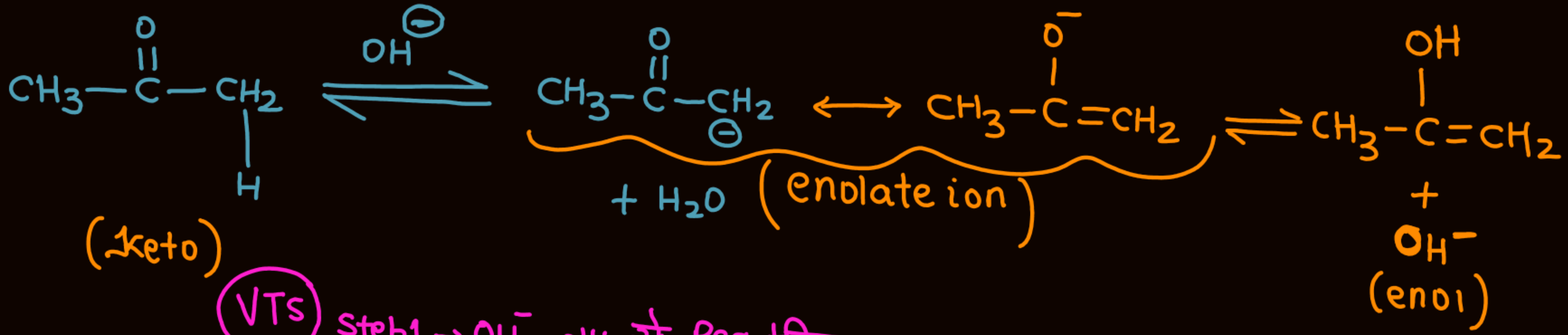
 ✓

Mechanism (keto-enol Tautomer)

Syllabus → Base Catalysed Tautomerism

Tautomerism → acidic as well as basic medium.
→ acid as well as base catalysed.

Catalyst → species which is not consumed in a reaction. It speeds up/slows up a reaction



VTs

Step1 → OH^-, αH से React किया → H_2O बनाया & enolate ion बनाया

Step2 → enolate ion → Resonance करता है।

Step3 → H_2O से H^+ लेके enol बनता है।

* enol में oxygen का H → H_2O से मिलता है।

Types of Tautomerism

Syllabus
1. diad Tautomerism
2. Triad "
3. Space "

① diad Tautomerism → Transfer of acidic H b/w 2 atoms.

$$H-C\equiv N \rightleftharpoons \overset{\ominus}{C}\equiv \overset{\oplus}{N}-H$$

acidic H; sp; 1, 2

$$C\equiv N-H$$

③ Triad Tautomerism → Transfer of acidic H b/w 3 atoms.

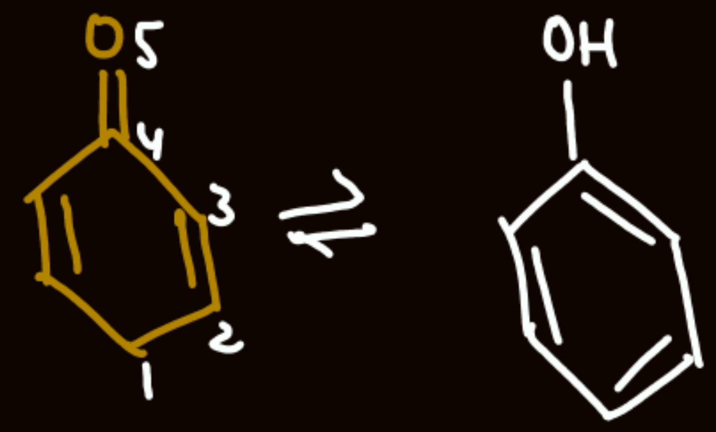
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CH_2$$

(3 O, 2 C, 1 CH_3)

④ Space Tautomerism →

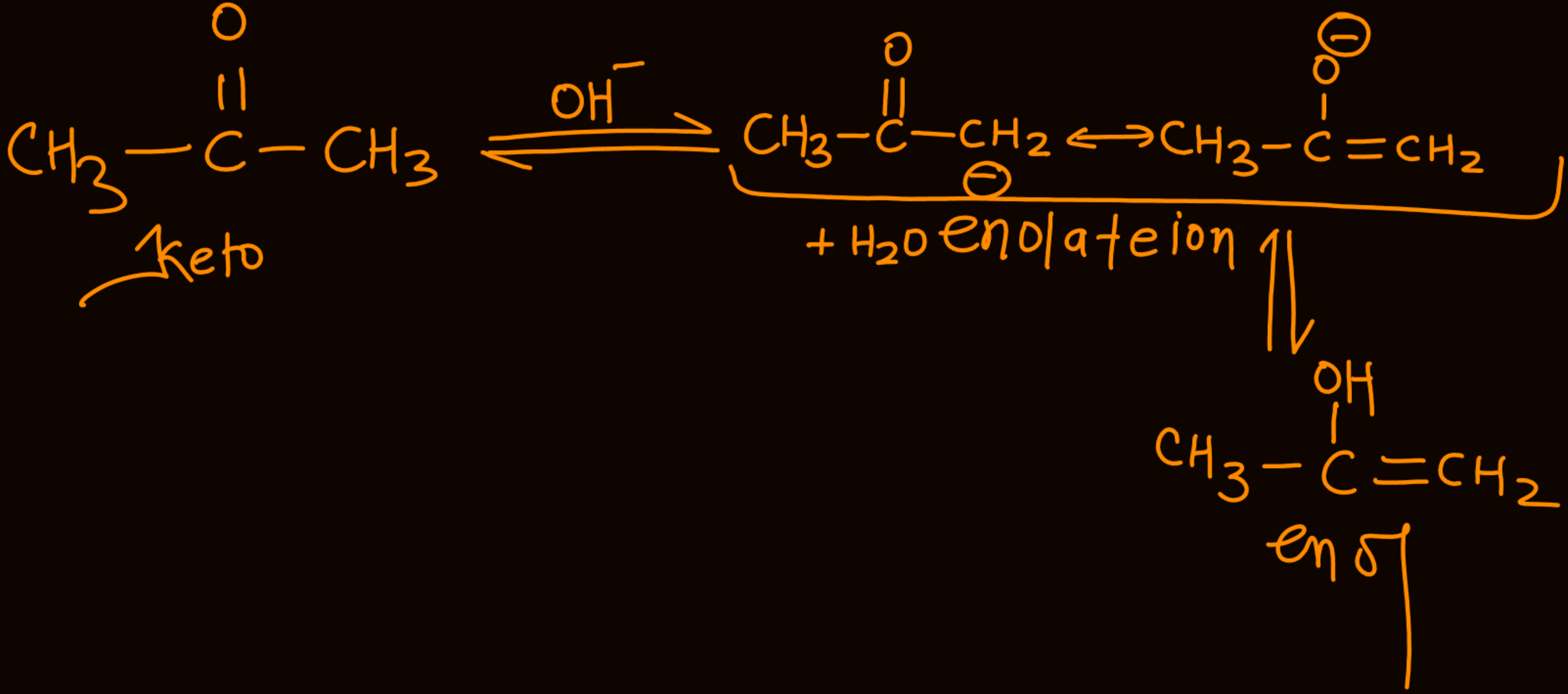
$$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_2=CH-CH=\overset{OH}{\overset{|}{C}}-H$$

(1, 2, 3, 4, O 5)



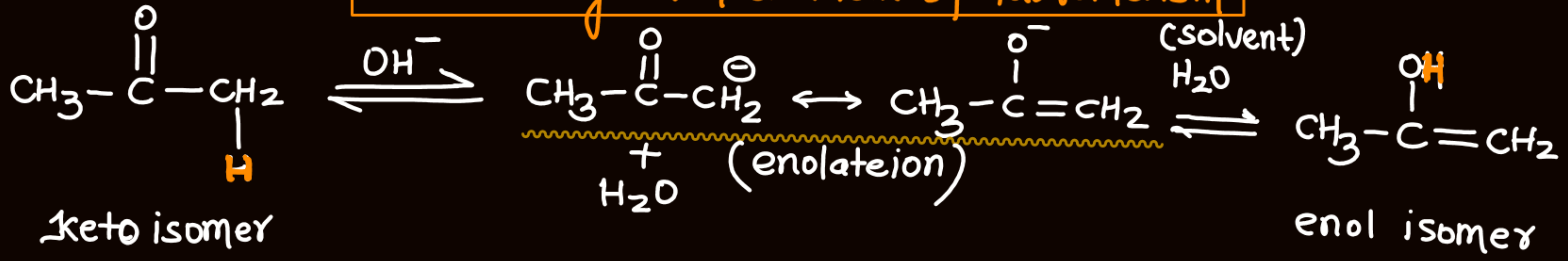
$$CH_3-CH=CH-CH=CH-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_2=CH-CH=CH-CH=\overset{OH}{\overset{|}{C}}-H$$

(1, 2, 3, 4, 5, 6, 7 O)

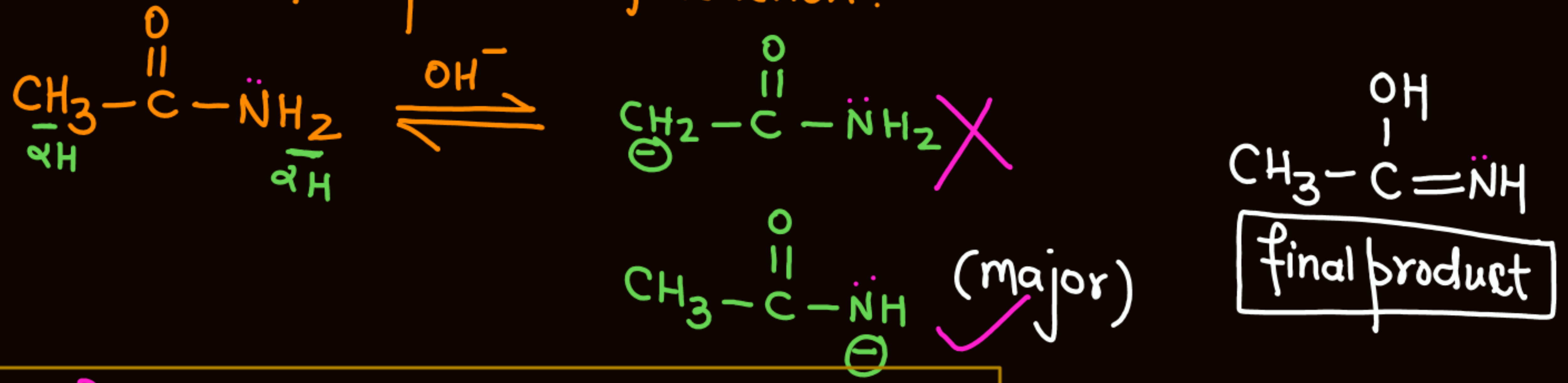


OH⁻
keto
+ H₂O
enolate ion
enol

Base Catalysed Mechanism of Tautomerism

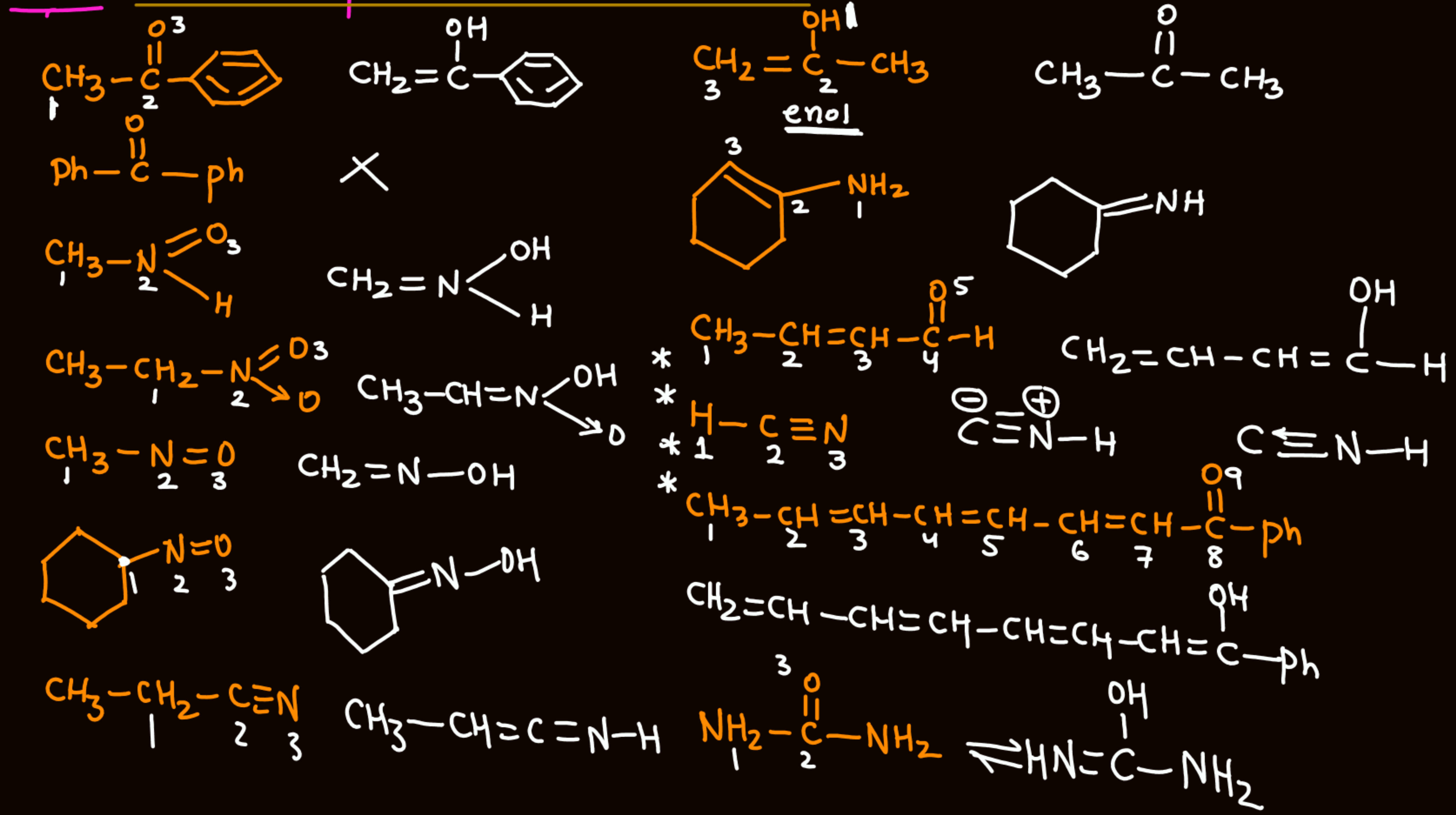


Que what will the final product of reaction :-



Note → Product of Tautomerism ∝ stability of anion

Que write the product of Tautomerism –



Special Tautomerism

Case (1)

$$\underset{1}{CH_3}-\underset{2}{N}{\overset{\nearrow O_3}{\underset{\searrow O}{}}} \rightleftharpoons CH_2=N{\overset{\nearrow OH}{\underset{\searrow O}{}}}$$

(nitro-acinitro Tautomerism)

nitro

aci nitro
(acidic nitro) ⟶ Soluble in NaOH

H is connected to More electronegative atom
So it is called aci-nitro.

note *: If nitro comp has acidic H (αH) then it is Soluble in NaOH. bcoz it will convert to acidic nitro.

Que Which of the following is Soluble in NaOH —

(1) 

(2) 

(3) $Ph-NO_2$

(4) CCl_3-NO_2

Case 2

nitroso-oxime Tautomerism

$$CH_3-CH_2-N=O \rightleftharpoons CH_3-CH=N-OH$$

Nitroso — Oxime (more acidic)

Case 3

Urea - IsoUrea Tautomerism

$$NH_2-\overset{\overset{O}{\|}}{C}-NH_2 \rightleftharpoons HN=\overset{\overset{OH}{|}}{C}-NH_2$$

Urea — Iso Urea (more acidic)

Comparison of enol Content / Stability order

* generally, keto is more stable than enol.

Keto ↓ $C=O$: Strong bond, More Stable

Enol ↓ $C=C$: weak bond, less stable

* But in some cases enol is more stable than keto.

(i) Aromaticity

(ii) H Bonding

(iii) Extended Resonance (atleast 2 π bond is in Resonance with lonepair)

Que

$CH_3-\overset{\overset{O}{||}}{C}-CH_3$ (a)

keto

$CH_2=\overset{\overset{OH}{|}}{C}-CH_3$ (b)

enol

a > b stability

Que



Keto   enol

Stability → b>a

Que

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

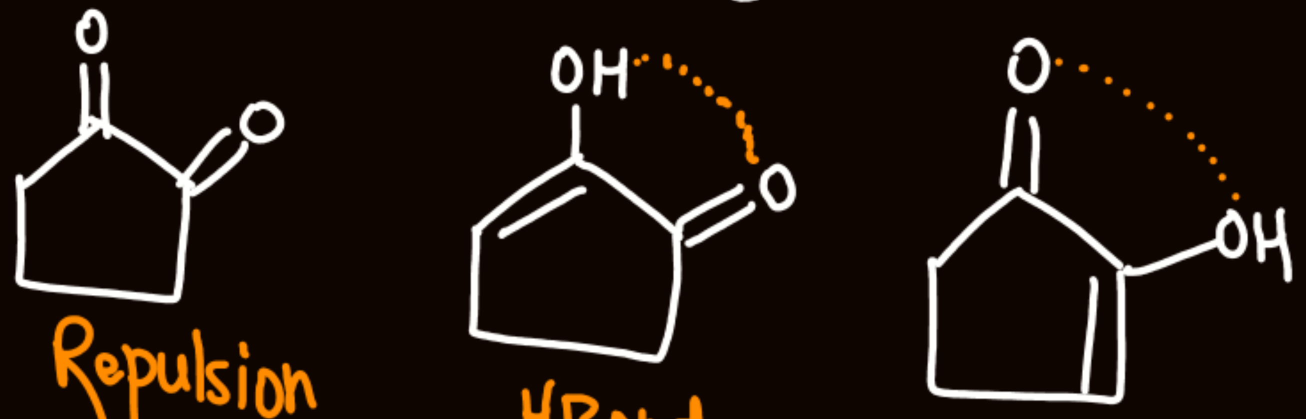
$$CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

Extended Reso + HBond

$$CH_2=\overset{OH}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

Stability → 2 > 1 > 3

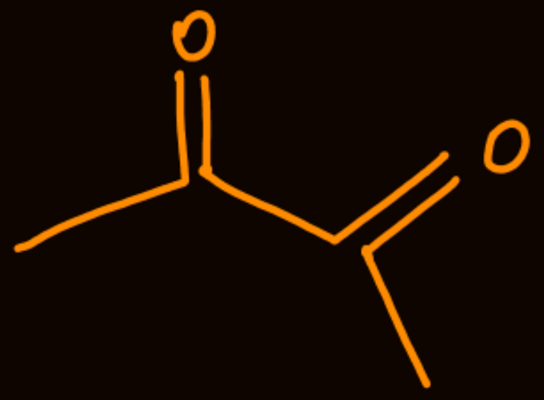
Que

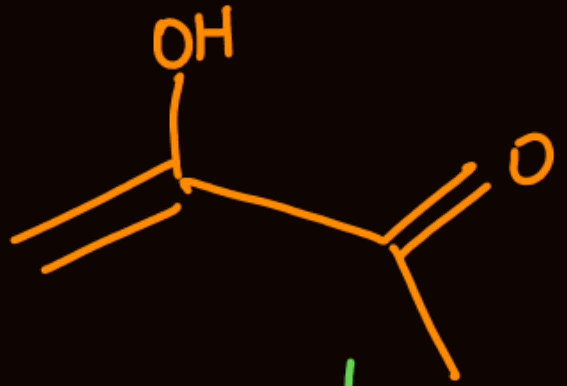


Repulsion   HBond Chelate Ring

Stab → 2>3>1

Q





Stab → I > II

Single Bond

↓

Free Rot^{n} Possible

↓

H Bond ✗

% of enol content / Enol Content

Enol Content ∝ acidic H

∝ Stab of anion

Q

$CH_3-\overset{O}{\overset{||}{C}}-CH_3$

$CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

acidic H

enol content

b > a

Q

$CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-H$

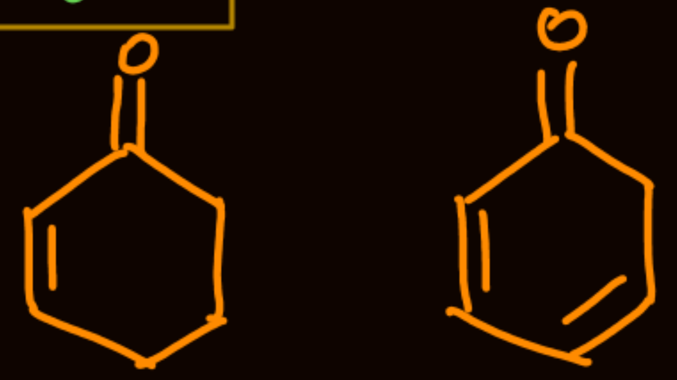
$CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

$CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-O-C_2H_5$

$C_2H_5-O-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-O-C_2H_5$

enolcontent a > b > c > d

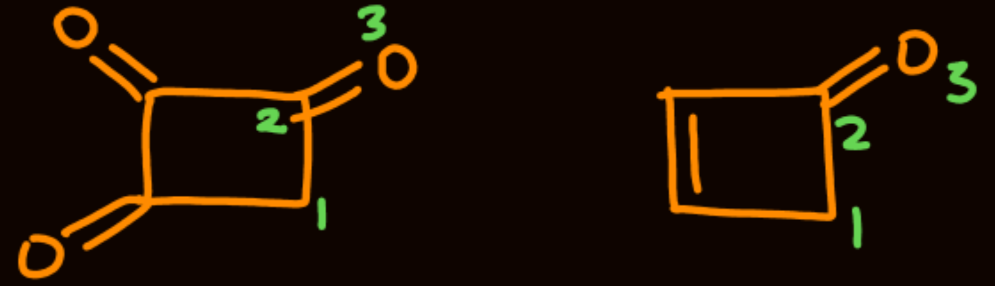
Q

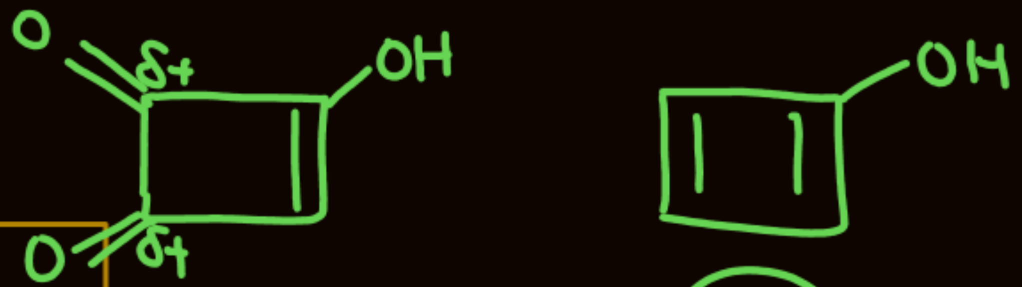


enol content

2 > 1

Q





Aromatic

AA

1 > 2 enol content

GOC | General Organic Chemistry | New Chapter

Formal charge

Charge on each Single atom (indivisual atom) in a molecule is called Formal charge.

Note → Sum of all formal charge in a molecule is called complete charge.

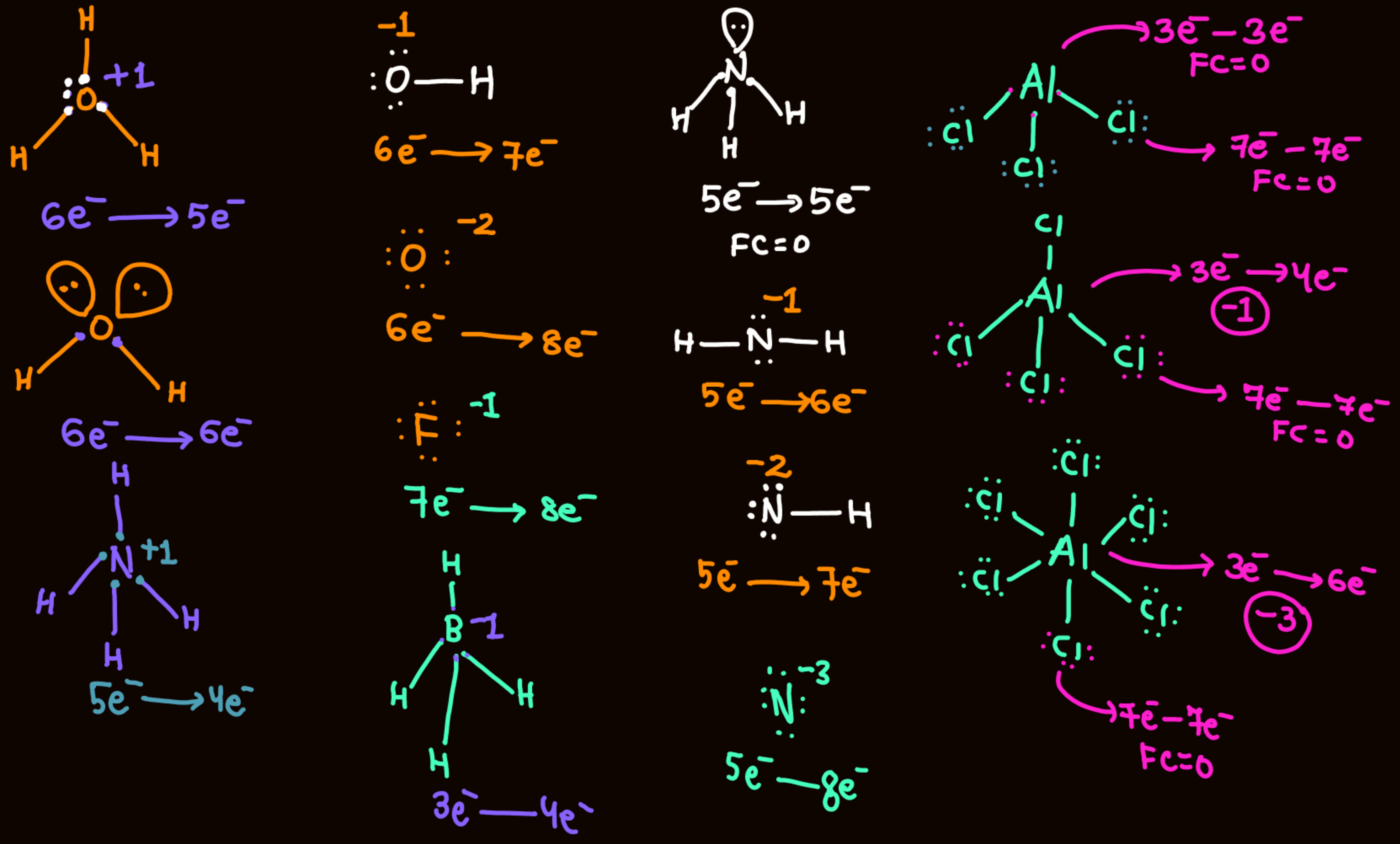
SO_4^{-2}



Valence electron electron

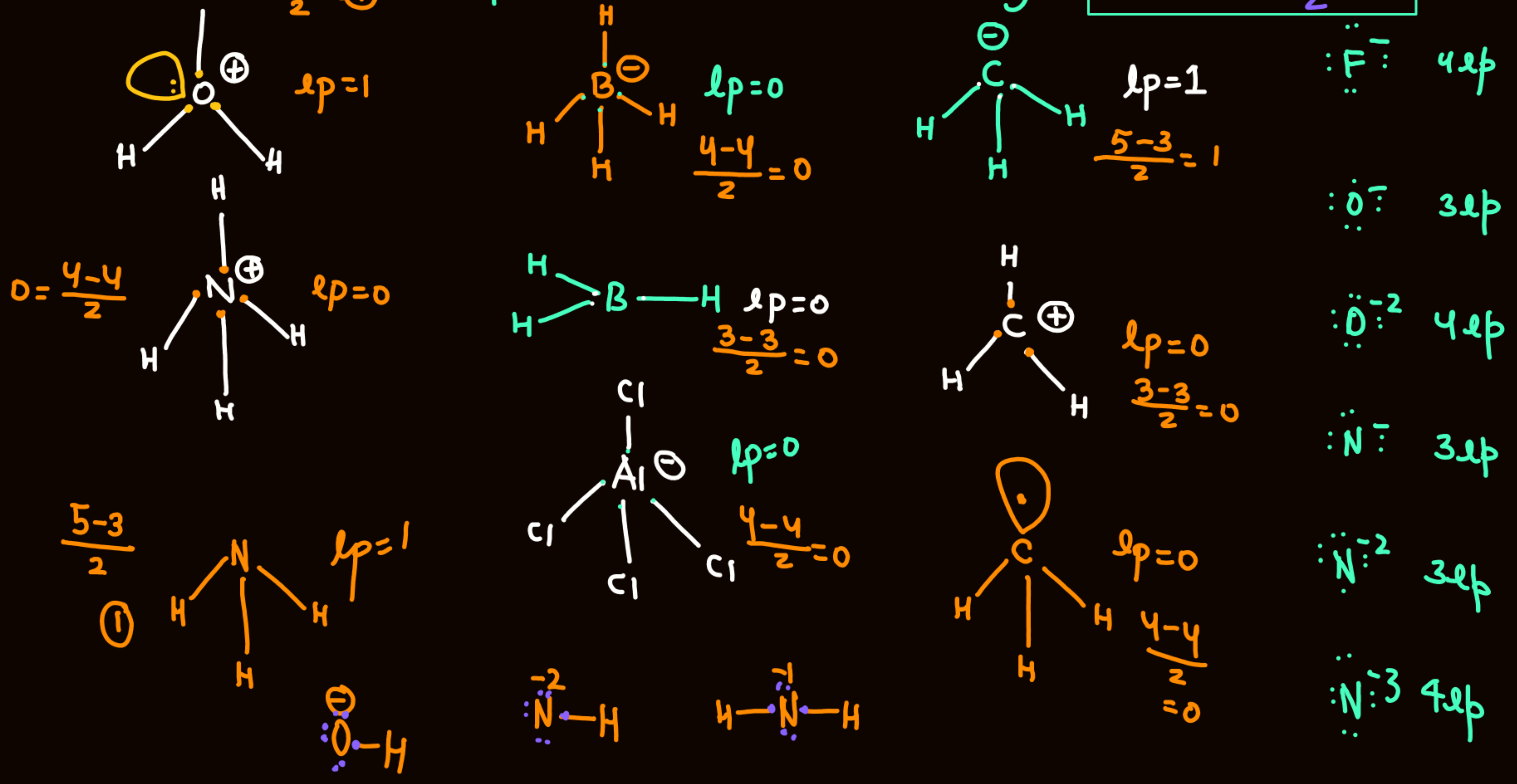
G13	G14	G15	G16	G17	G18
B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr
In	Sn	Sb	Te	I	Xe
Tl	Pb	Bi	Po	At	Rn

:He


+1
6e⁻ → 5e⁻
6e⁻ → 6e⁻
+1
5e⁻ → 4e⁻
-1
6e⁻ → 7e⁻
-2
6e⁻ → 8e⁻
-1
7e⁻ → 8e⁻
-1
3e⁻ — 4e⁻
5e⁻ → 5e⁻
FC=0
-1
5e⁻ → 6e⁻
-2
5e⁻ → 7e⁻
-3
5e⁻ — 8e⁻
3e⁻ — 3e⁻
FC=0
7e⁻ — 7e⁻
FC=0
3e⁻ → 4e⁻
-1
7e⁻ — 7e⁻
FC=0
3e⁻ → 6e⁻
-3
7e⁻ — 7e⁻
FC=0

Lone pair Calculation with Formal Charge

$$\text{lone pair} = \frac{Ve^- - \text{bond}}{2}$$



Organic Reaction

Old bonds are broken & new bonds are formed, this is k/a organic reaction.

- Old bonds are broken → Reactant (Bond clevage)/(Bond Fission)
- New bonds are formed → Product

$$\overset{\delta+}{CH_3}-\overset{\delta-}{Cl} + \overset{\oplus}{K}\,\overset{\ominus}{OH} \longrightarrow CH_3-OH + KCl$$

- CH_3-Cl: Covalent comp
- KOH: Ionic comp

Reactant: Bond cleavage / Bond fission

Product: new bonds are formed.

Reactant → Substrate, Reagent

Substrate: Molecule on which Reagent attacks is called Substrate. (must be organic molecule)

Reagent: Molecule which attacks on substrate is called Reagent. (May be organic/inorganic molecule)

Substrate = CH_3-Cl
Reagent = KOH

Reagent (attacking species)

Electrophile (E^+)

Electron Lover

-ve charge Lover

1. +ve charged species
2. electron deficient species
   - ↳ octet incomplete
     - ↳ Hypovalent species
3. Vacant orbital

H^+, Cl^+, Br^+, $\overset{+}{SO_3H}$, $\overset{\delta+}{CH_3}-OH$, $R-\overset{O}{\overset{\|}{\underset{\delta+}{C}}}-H$,

BF_3, BH_3, BCl_3, $AlCl_3$, $ZnCl_2$, $PbCl_2$, $PbCl_4$, $SnCl_2$, $SnCl_4$

$R-\overset{O}{\overset{\|}{\underset{\delta+}{C}}}-OH$, $\underset{\delta+}{R}-NH_2$, $R-\overset{O}{\overset{\|}{\underset{\delta+}{C}}}-Cl$, $R-\overset{O}{\overset{\|}{\underset{\delta+}{C}}}-NH_2$, $\overset{\oplus}{C}H_3$

Nucleophile (Nu^-)

Nucleus Lover

+ charge Lover

1. -ve charged species
2. electron rich species
   - ↳ octet complete
   - & having lonepair / -ve charge

H^-, Cl^-, Br^-, COO^-, NH_2^-, NH^{-2}, N^{-3}, OH^-, O^{-2}

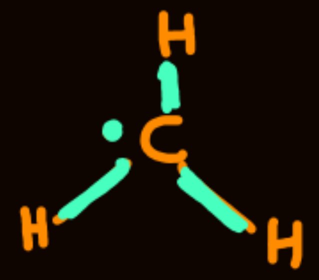
F^-,

$\ddot{N}H_3$, $R\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$, $\ddot{O}H_2$, CH_3^-,

$RMgX$ (R^-), R_2Zn (R^-), R_2CuLi (R^-), $LiAlH_4$ (H^-), $NaBH_4$ (H^-), NaH (H^-)

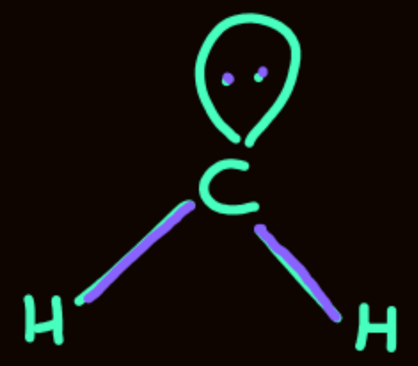
Note → Free Radical, Carbene ($:CH_2$) are electrophiles.

$\dot{C}H_3$



$7e^-$

Octet incomplete



$6e^-$

Octet incomplete

Que H_3O^+ & NH_4^+ are –

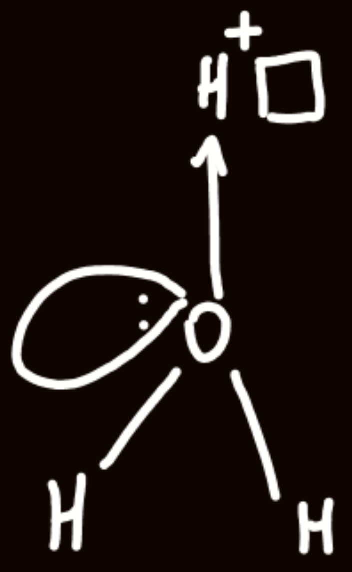
(a) E^+, Nu^-

(b) Nu^-, E^+

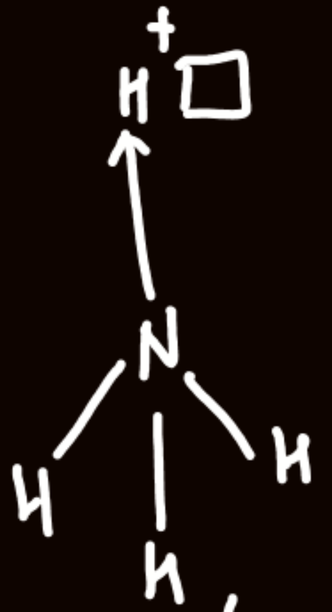
(c) E^+, E^+

(d) Nu^-, Nu^-

(e) Neither E^+ nor Nu^- ✓

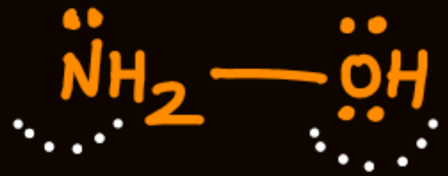


octet complete



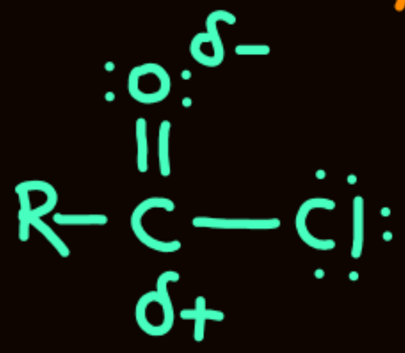
octet complete

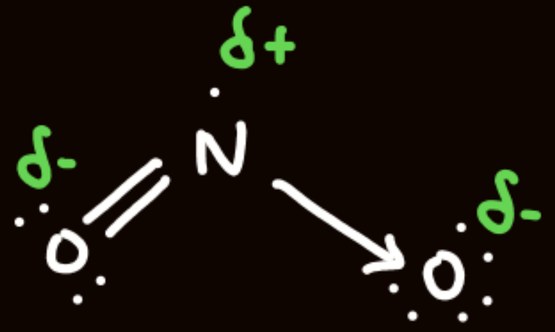
Ambidentate nucleophile → Nucleophile having more than one donor sites.

 , 

Ambiphile → Behaves as electrophile and nucleophile both.







Bond clevage | Bond Fission | Bond Breaking

Homolytic Bond Fission

$$A{\bullet}\!-\!{\bullet}B \xrightarrow{\Delta} A\bullet + B\bullet$$

Equal distribution of bonded electron.

Both atom have same EN.

$\Delta EN = 0$

$\Delta EN \approx 0$ (~ 0.4)

$$Cl{\bullet}\!-\!{\bullet}Cl \xrightarrow{\Delta} Cl\bullet + Cl\bullet$$

$$F{\bullet}\!-\!{\bullet}F \xrightarrow{\Delta} F\bullet + F\bullet$$

$$H{\bullet}\!-\!{\bullet}H \xrightarrow{\Delta} H\bullet + H\bullet$$

$$C{\bullet}\!-\!{\bullet}H \longrightarrow C\bullet + H\bullet$$

C: 2.5, H: 2.1, $\Delta EN = 0.4$

Free Radical is formed.

Heterolytic Bond Fission

$$A-B \xrightarrow{\Delta} A{:} + B$$

$$A + B{:}$$

Unequal distribution of Bonded electron.

Both have different EN.

$\Delta EN \neq 0$

$\Delta EN \geq 0.5$

$$\overset{\delta+}{H}-\overset{\delta-}{Cl} \xrightarrow{\Delta} H^{\oplus} + Cl{:}^{\ominus}$$

H: 2.1, Cl: 3.0

$$C-Cl \xrightarrow{\Delta} C^{\oplus} + Cl{:}^{\ominus}$$

C: 2.5, Cl: 3.0

$$H-F \xrightarrow{\Delta} H^{\oplus} + F{:}^{\ominus}$$

H: 2.1, F: 4.0

Cation & Anion formation takes place.

Condition of Homolytic clevage

1. High Temp (≥500°c)
2. hν / Sunlight / Prolonged Heating
3. presence of peroxide
4. nonpolar Substrate (ΔEN=0)
5. nonpolar Solvent

Condition of Heterolytic clevage

1. Low temp
2. polar Substrate (ΔEN ≠ 0)
3. polar Solvent

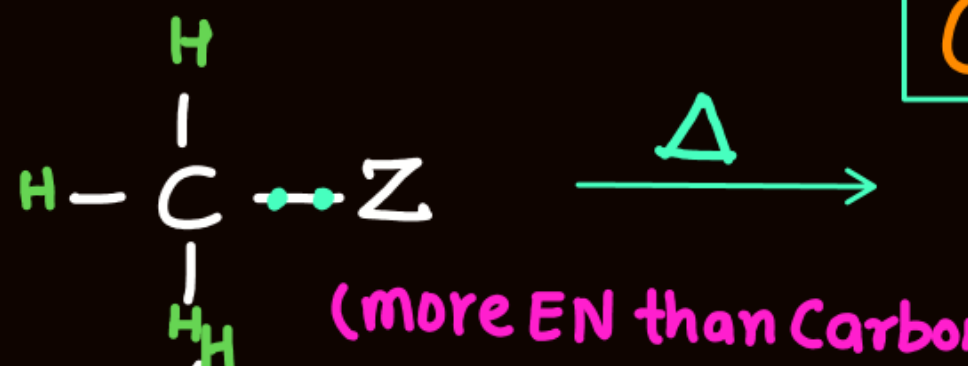
Reaction Intermediate

Unstable species which are formed after the start of Reaction & gets finished before completion of reaction are k/a Reaction Intermediate.

1. carbocation
2. Carbanion
3. FreeRadical
4. Carbene ← syllabus) Rimer Tieman Reaction
5. nitrene
6. Benzyne

(5) and (6): not in Syllabus

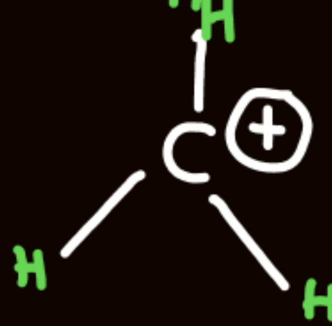
Carbocation

#1 

(more EN than Carbon)

(Heterolytic clevage)

Lewis Acid → acceptor
Lewis Base → donor
→ Electrophile (only when vacant orbital is present)
→ nucleophile

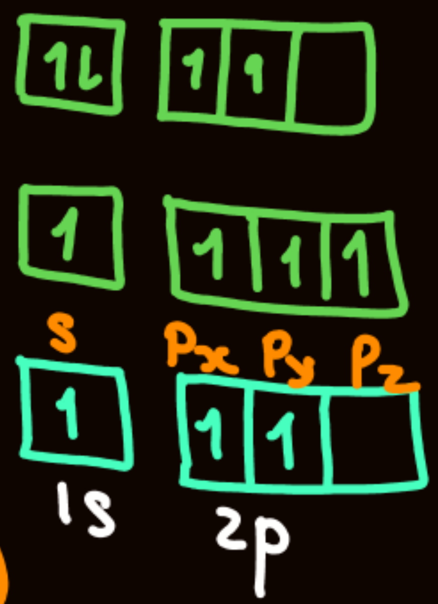
#2 

→ 3σ bond, 0 lonepair, 1 Vacant orbital, Formal charge = +1,
(1σ → 2s
2σ → 2p)

Ground State (6) C → $1s^2\ 2s^2\ 2p^2$

excited state C^* →

C^+ →

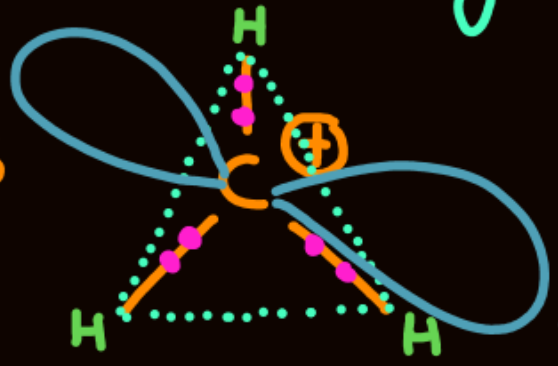


#3 Hybridization = Sp^2 (120°)

#4 Geometry | Shape = Trigonal planar

#5 

Vacant p orbital in carbocation is perpendicular to plane.

#6 

→ $6e^-$
→ octet incomplete
→ e^- deficient
→ Electrophile
→ Lewis Acid

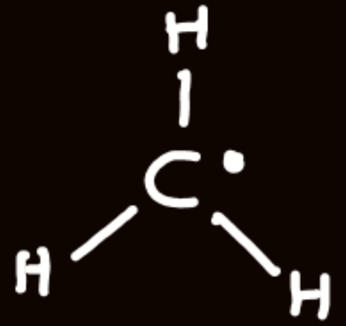
#7 Carbocation is diamagnetic.
↓
all electrons are Paired

Carbon Free Radical

#1 $H_3C{-}Z \xrightarrow{\Delta} H_3C\cdot + Z\cdot$ (Homolytic clevage)

(C & Z have Same EN)

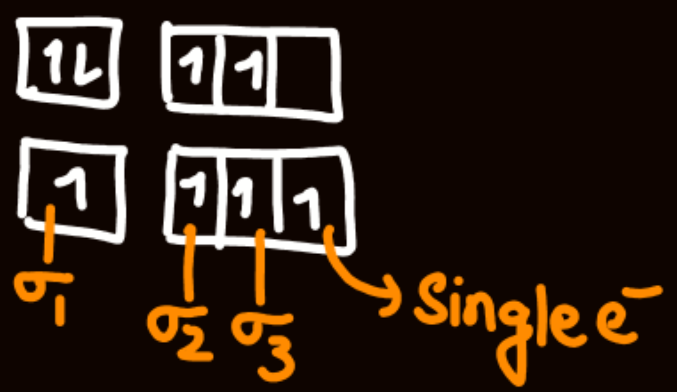
#2



→ 3σ bond, 0 lonepair, 1 Single electron, 0 Vacant orbital, Formal charge = 0

C → $1s^2 2s^2 2p^2$

C*



#3 Hybridization → sp^2 (120°)

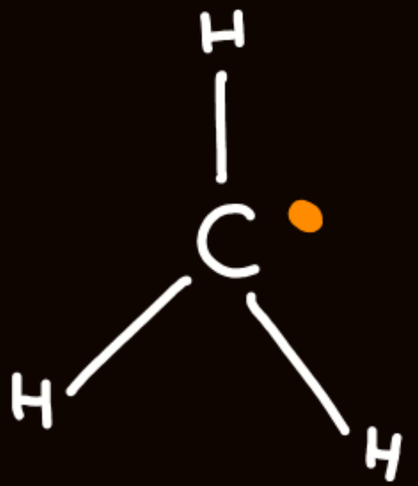
#4 Geometry | shape → Trigonal planar

#5



→ Single Free e⁻ is lying perpendicular to plane.

#6

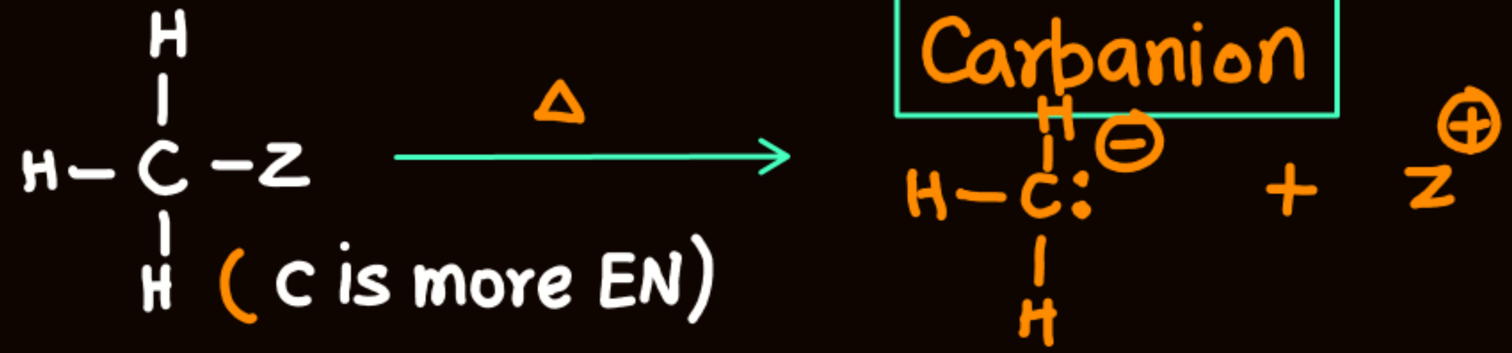


→ 7e⁻
→ octet incomplete
→ electron deficient
→ Lewis Acid ✗
→ Electrophile ✗

#7 Free Radical is paramagnetic.

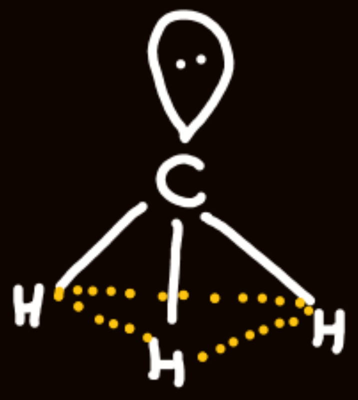
#8 → neither Electrophile nor nucleophile
neither Lewis Acid nor Lewis base.

Carbanion

#1 

(C is more EN)

(Heterolytic Clevage)

#2 

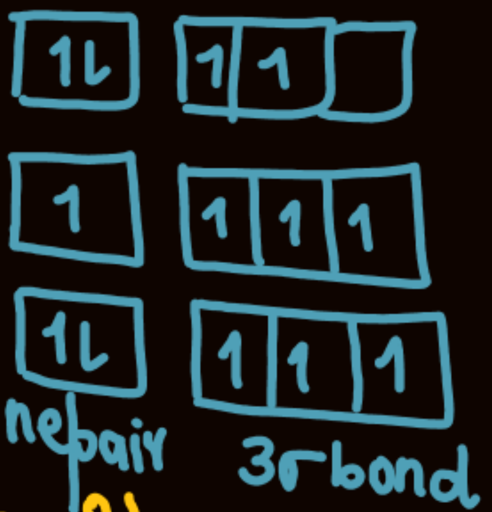
→ 3σ bond, 1 lonepair, 0 Vacant orbital, Formal charge = −1

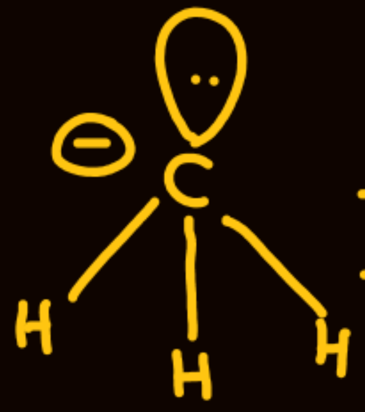
- 3σ bond ↓ (3σ → 2p orbital)
- 1 lonepair ↓ sp^3 hybrid orbital

#3 C → $1s^2 2s^2 2p^2$

C*

$C^{\ominus}$ →





- → $8e^-$
- → octet complete
- → electron rich species
- → nucleophile
- → Lewis base

Hybridization → sp^3 (109.5°)

Geometry → Tetrahedral (lonepair के साथ)

Shape → pyramidal (lonepair के बिना)

diamagnetic

note → Carbanion has sp^3 hybridization

BUT

If Carbanion is in Resonance then it has sp^2 hybridisation.

Electronic displacement effect

Complete Shifting of electron or partial shifting of electron is k/a e^- displacement Effect.

e^- → Partial shifting

e^- → Complete shifting

1. Inductive Effect
2. Resonance Effect / Mesomeric Effect
3. Hyperconjugation effect
4. Electromeric Effect
5. Inductomeric Effect (not in Syllabus)

Inductive Effect (Sigma electron)

Partial shifting of Sigma electron towards more electronegative atom in a Sigmabond.

eg → $\overset{\delta+}{H_3C}$ —→ $\overset{\delta-}{Cl}$ (More EN) $\overset{\delta+}{H_3C}$ —→ $\overset{\delta-}{F}$ (more EN) CH_3 —→ $\overset{\delta-}{I}$ (more EN)

Inductive Effect

$$\underset{C}{\delta\delta\delta\delta+} \rightarrow \underset{C}{\delta\delta\delta+} \rightarrow \underset{C}{\delta\delta+} \rightarrow \underset{C}{\delta+} \rightarrow \underset{Z}{\delta-}$$

More EN

$$\underset{C}{\delta\delta\delta\delta-} - \underset{C}{\delta\delta\delta-} \leftarrow \underset{C}{\delta\delta-} \leftarrow \underset{C}{\delta-} \leftarrow \underset{Z}{\delta+}$$

less EN

$$|\delta+| > |\delta\delta+| > |\delta\delta\delta+| > |\delta\delta\delta\delta+|$$

$$|\delta+ + \delta\delta+ + \delta\delta\delta+ + \delta\delta\delta\delta+| = |\delta-|$$

$$|\delta-| > |\delta\delta-| > |\delta\delta\delta-| > |\delta\delta\delta\delta-|$$

$$|\delta- + \delta\delta- + \delta\delta\delta- + \delta\delta\delta\delta-| = |\delta+|$$

Partial & parmament shifting of Sigma electrons towards more EN atom is called Inductive effect.

Reason of Inductive effect → Electronegativity.

Inductive effect is distance dependent effect.

$$\text{Inductive effect} \propto \frac{1}{\text{distance}}$$

Inductive effect is valid upto 3 Carbon & it is almost zero at 4th Carbon.

It is only applicable in Sigma bond and not in pi bond.

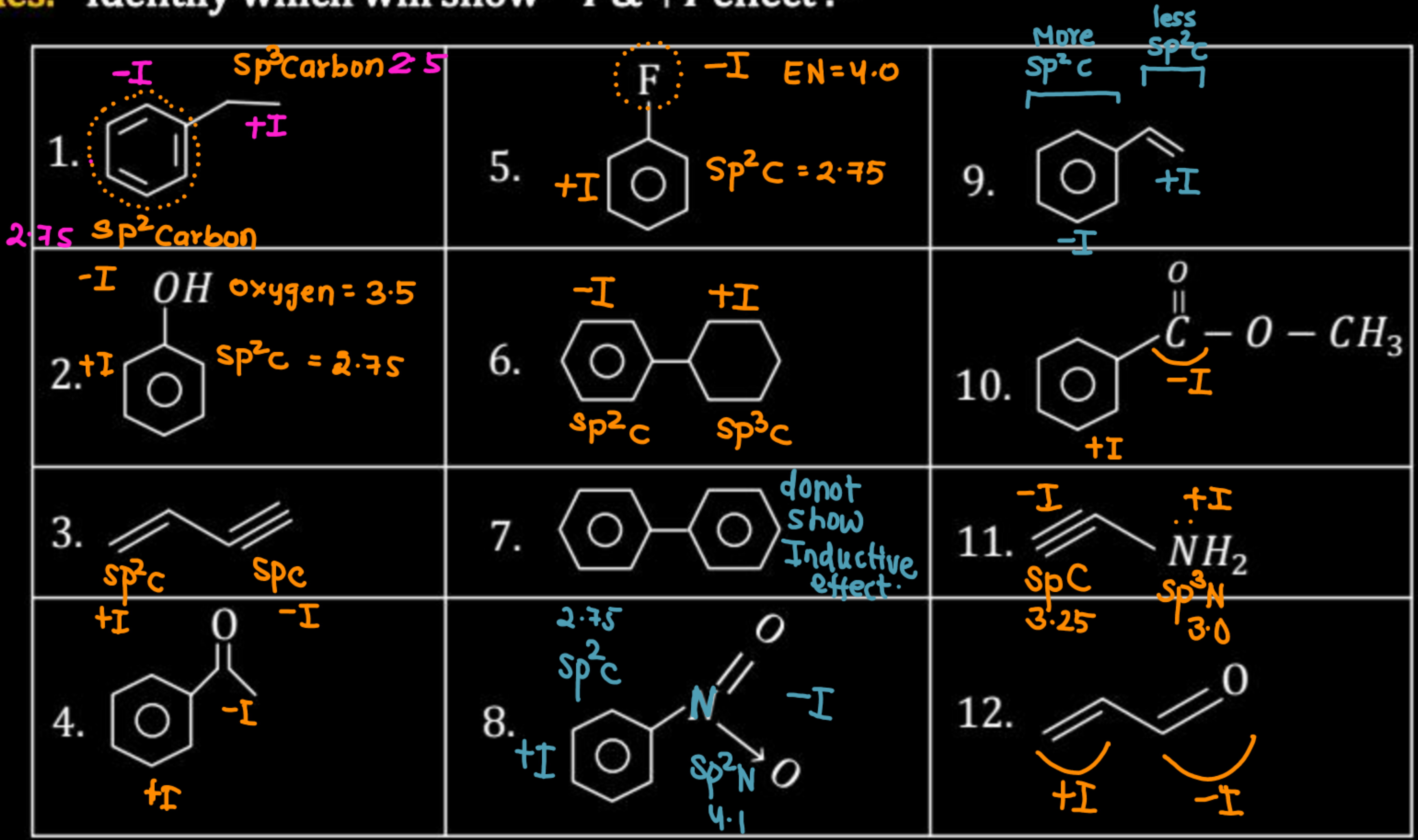
Type of Inductive Effect

−Inductive effect	+Inductive effect
−I effect	+I effect
electron withdrawing group	electron donating group
More EN atom	Less EN atom
	Electron Rich atom (−ve charge, lonepair)

EN order: sp N 5.1, sp^2 N 4.1, sp^3 N 3.0

EN order → spC > sp^2C > sp^3C
3.25 > 2.75 > 2.50

Ques. Identify which will show $-I$ & $+I$ effect :-



−Inductive effect ∝ EN

Ques. Which of the following show more inductive effect ?

−I 1. $-F > -Cl > -Br > -I$

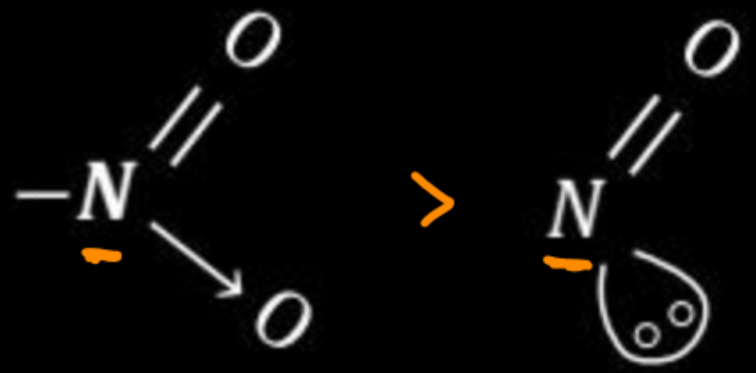
−I 2. $-OH > -SH$

−I 3. $-OCH_3 > -SCH_3$

−I 4. $-NH_2 > -PH_2$

−I 5. $-CF_3 > -CCl_3 > -CBr_3 > -CI_3$

6. $-C \equiv N > -CH = NH_2$

7. 

H	B	C	N	O
2.1	2.0	2.5	3.0	3.5
			P 2.1	S 2.5

F — 4

Cl — 3.0

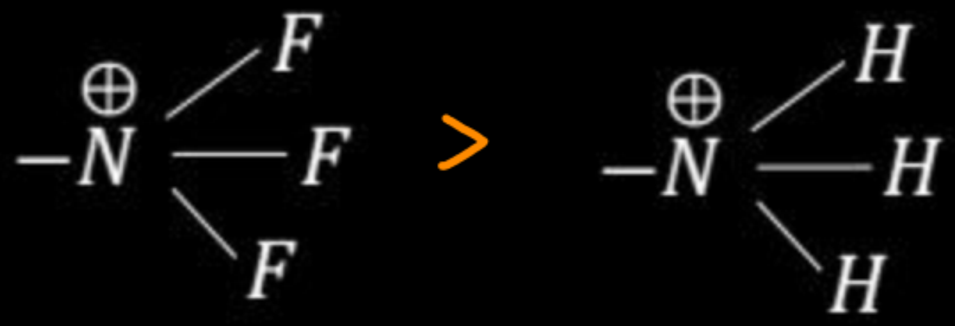
Br — 2.8

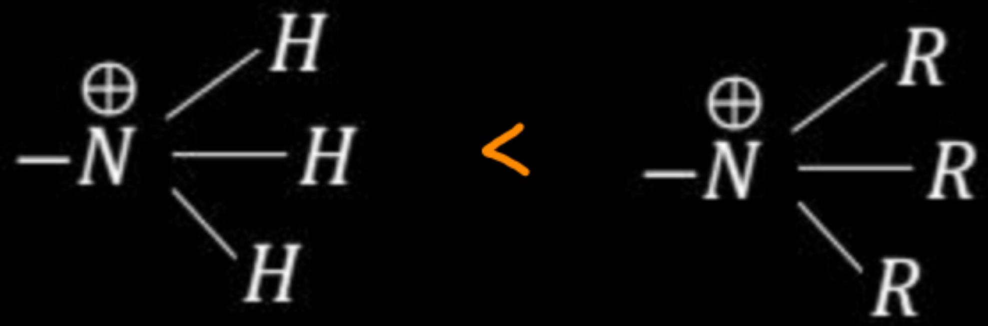
I — 2.5

Ques. Which of the following show more inductive effect ?

8. $-\overset{O}{\overset{\|}{C}}-H$ < $-\overset{O}{\overset{\|}{C}}-Cl$

9. $-C\equiv CH$ > $-CH=CH_2$

10. 

11. 

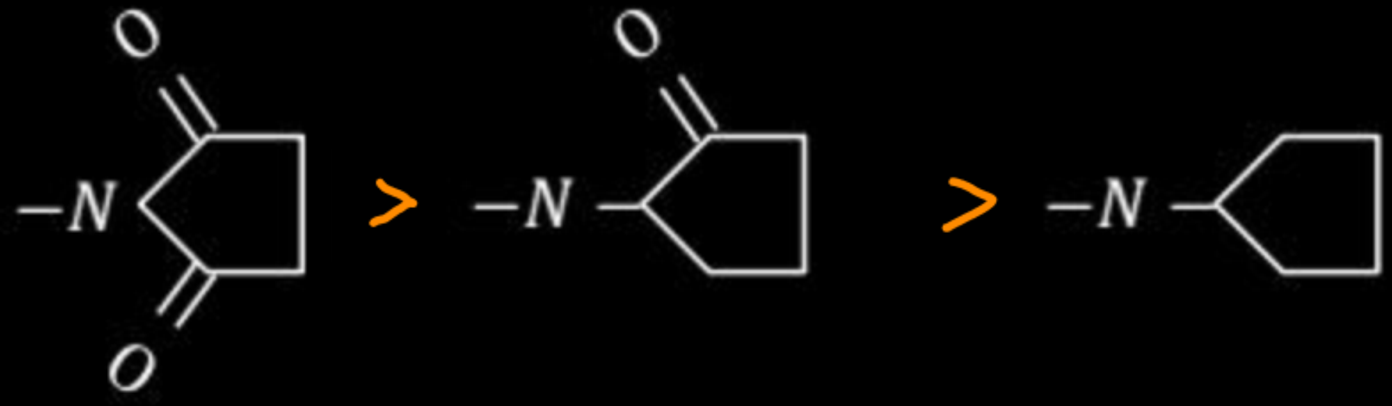
N••—H
2p 1s
Small bond

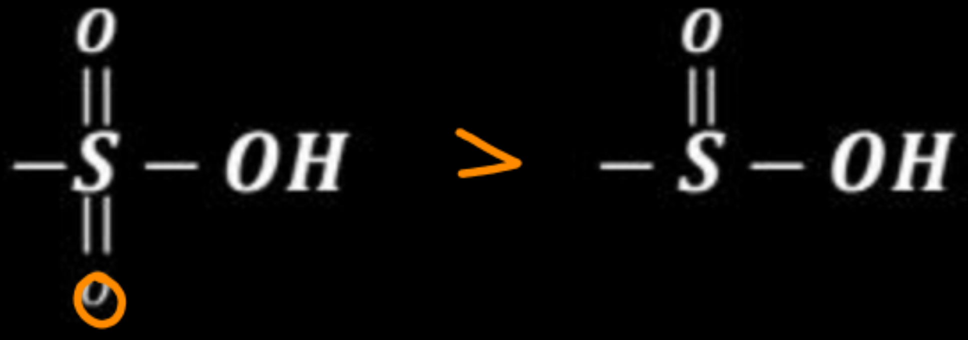
<

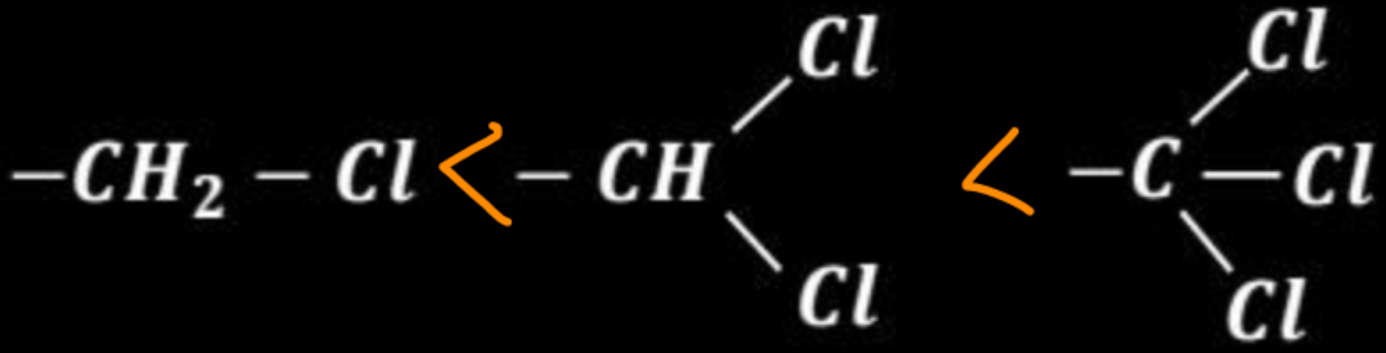
N-••—C
2p 2p
Large bond
e⁻ away from N
e⁻ की कमी
-I

12. $-CH=CH_2$ < 

Ques. Which of the following show more inductive effect ?

13. 

14. 

15. 

Ques. Which of the following show more inductive effect? , $\overset{1}{H}$–H , $\overset{2}{H}$–D , $\overset{3}{H}$–T

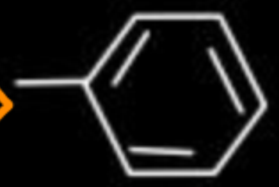
+I 16. $-CH_3 < -CH_2-CH_3 < -CH_2-CH_2-CH_3$

Cannot donate easily ↑ C–H < C–D < C–T (+I) ↑ donate easily

Large bond (Vibration more) (Light isotope) — Small bond (Vibration less) (Heavy isotope) (carbon का e⁻ carbon के पास है)

+I 17. $-CH_3 < -CH_2D < -CHD_2 < -CD_3$

+I 18. $-CH_3 < -CH_2-CH_3 < -CH(CH_3)_2 < -C(CH_3)_3$

−I 19. $-C\equiv CH$ (sp C) >  (sp² C) > $-CH=CH_2$ (sp² C) > $-CH_2-CH_3$ (sp³ C)

Ques. Which of the following show more inductive effect ?

−I 20. $-C \equiv CH$ > $-\ddot{N}H_2$

Sp Carbon 3.25 — Sp^3 N 3.0

21. $-CH = CH_2$ < $-\ddot{N}H_2$

Sp^2 C 2.75 — Sp^3 N 3.0

22.  < $-\ddot{N}H_2$

Sp^2 C 2.75 — Sp^3 N 3.0

23. $-C \equiv CH$ < $-N = CH_2$

Sp C 3.25 — Sp^2 N 4.1

Order of –I & +I

Order of –I

$H_3\overset{+}{O} > -\overset{+}{N}F_3 > -\overset{+}{N}R_3 > -\overset{+}{N}H_3 > -NO_2 > -C\equiv N > -SO_3H > -\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}-R$

(ना Farhan, ना Ritick, ना Himesh, ना ompuri, कौन, सोया, aldehyde, Ketone के साथ)

$-\overset{O}{\overset{\|}{C}}-OH > -\overset{O}{\overset{\|}{C}}-OR > -\overset{O}{\overset{\|}{C}}-NH_2 > -F > -Cl > -Br > -I > -OR > -OH$

(acid, Ester के साथ, amide, Halide के साथ, ether, alcohol)

$-C\equiv CH > -NH_2 > -Ph > -CH=CH_2$

(triple, नदी, फिर, double)

Order of +I

$-\overset{\ominus}{C}H_2 > -\overset{\ominus}{N}H > -\overset{\ominus}{O} > -\overset{O}{\overset{\|}{C}}-\bar{O} > -\underset{CH_3}{\overset{CH_3}{C}}-CH_3 > -\overset{CH_3}{CH}-CH_3 > -CH-CH_3 > -CT_3 > -CD_3 > -CH_3$

(At no=6, At no=7, At no=8; 3°, 2°, 1°; T, D, H)

Application of Inductive Effect

① Stability of Carbocation (CH_3^+) $\propto$ $+I$ $\propto$ $\frac{1}{-I}$

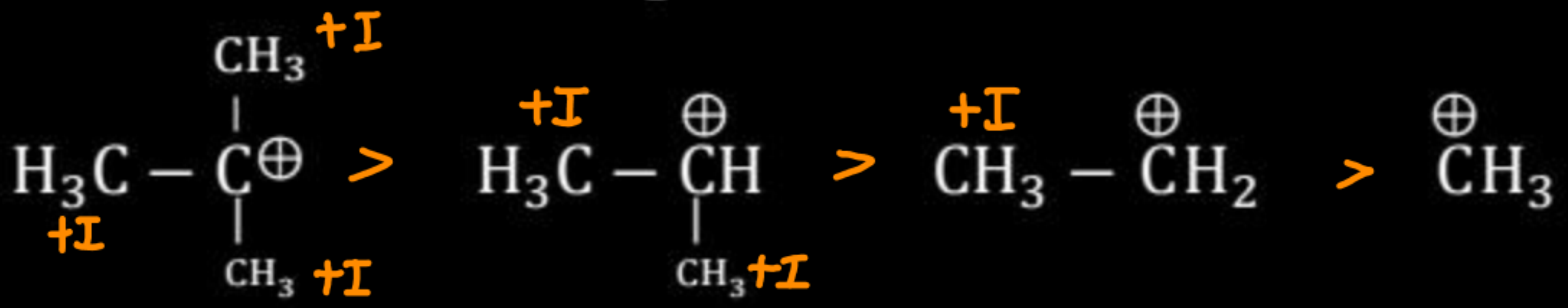
② Carbanion (CH_3^-) $\propto$ $-I$ $\propto$ $\frac{1}{+I}$

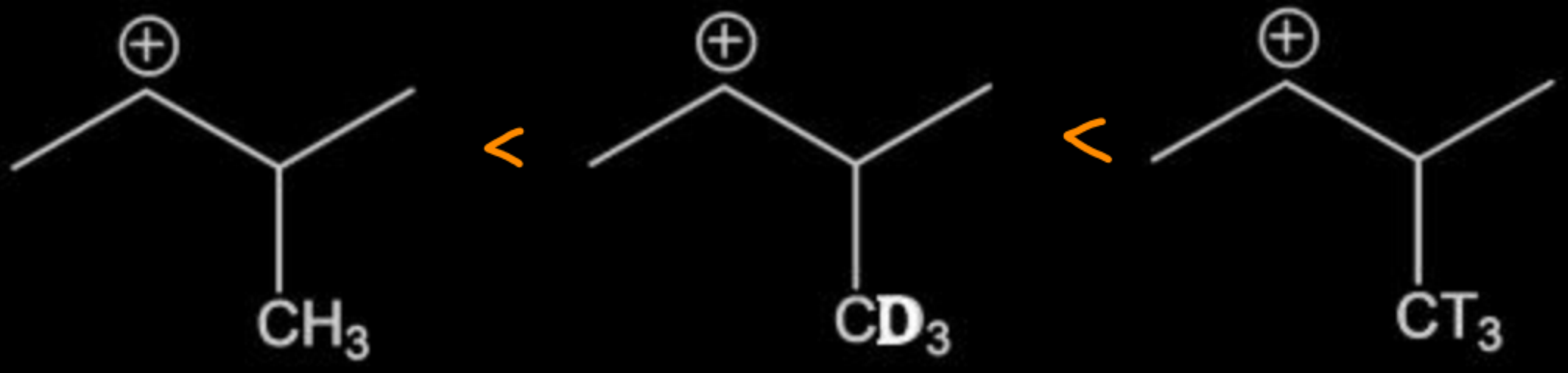
③ Free Radical ($\dot{C}H_3$) $\propto$ $+I$ $\propto$ $\frac{1}{-I}$

④ Acidic Strength $\propto$ Stability of Carbanion $\propto$ $-I$ $\propto$ $\frac{1}{+I}$

⑤ Basic Strength $\propto$ Stability of Carbocation $\propto$ $+I$ $\propto$ $\frac{1}{-I}$

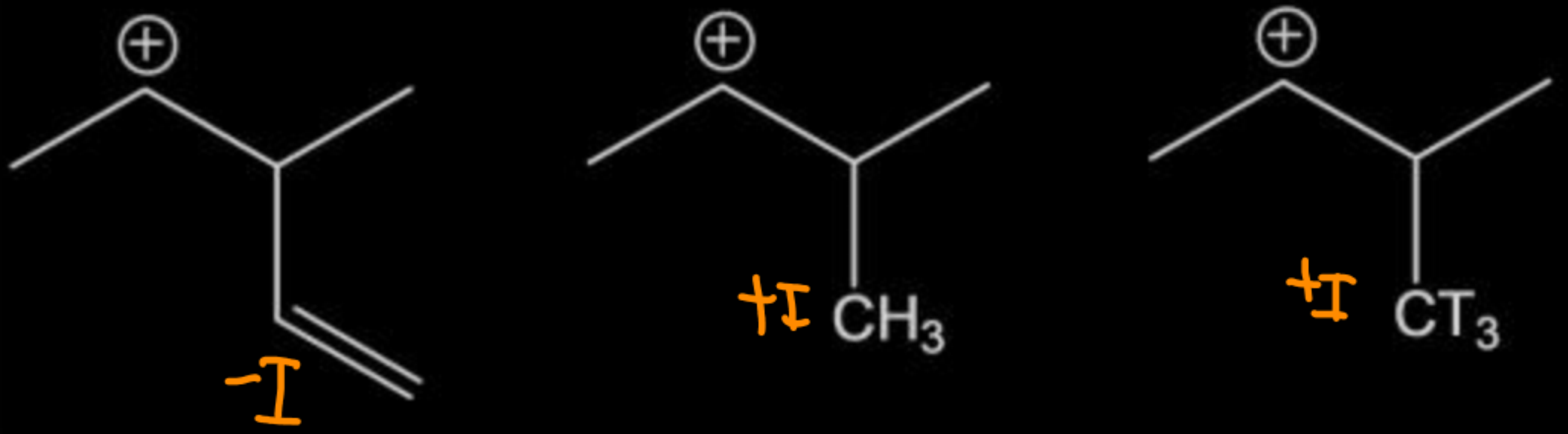
Ques. Which of the following carbocation is more stable?





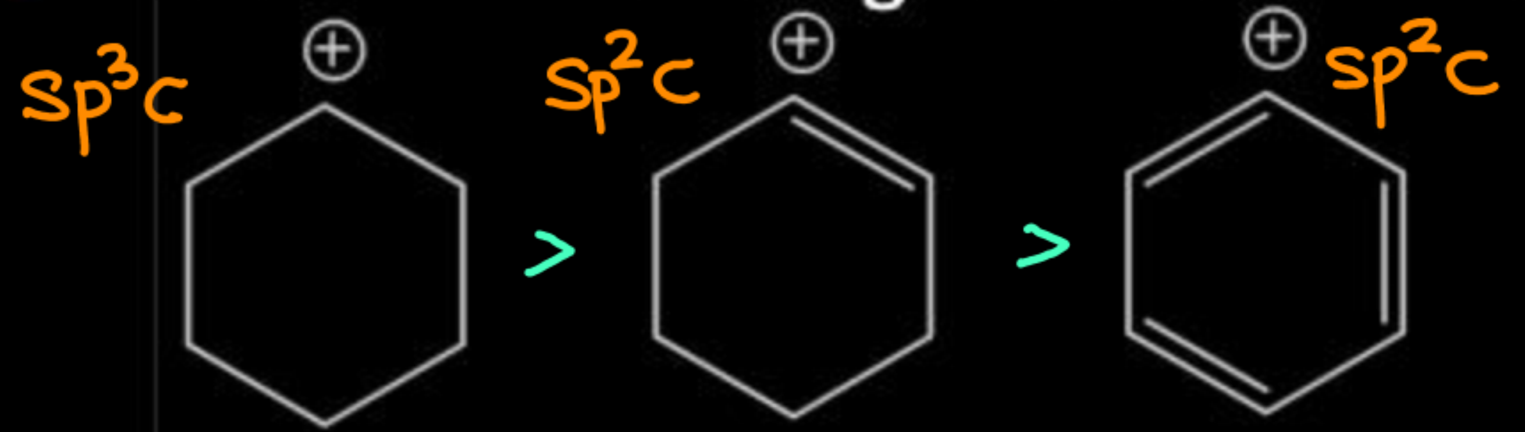
c > b > a





c > b > a

Ques. Which of the following carbocation is more stable?

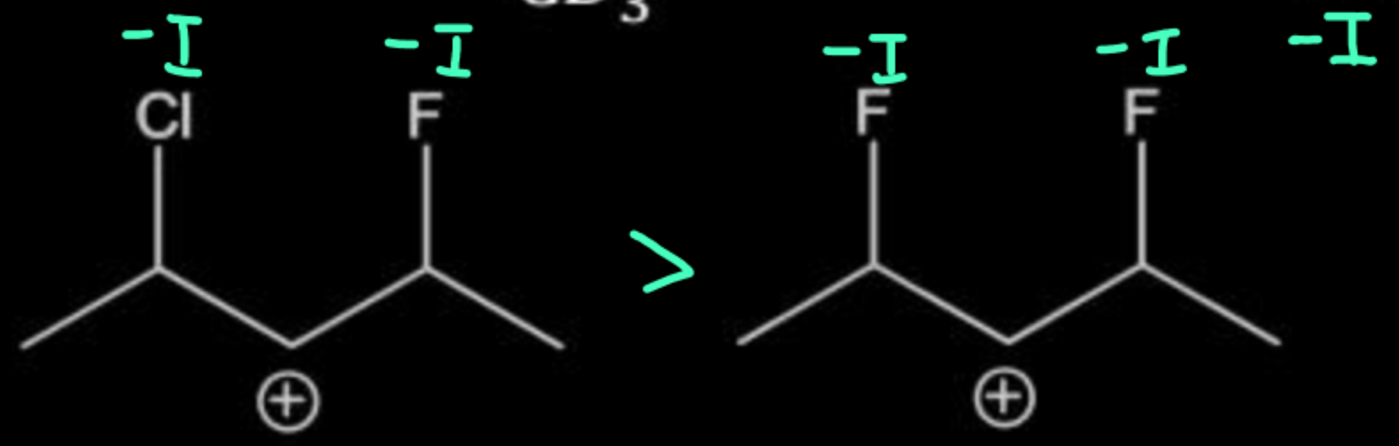


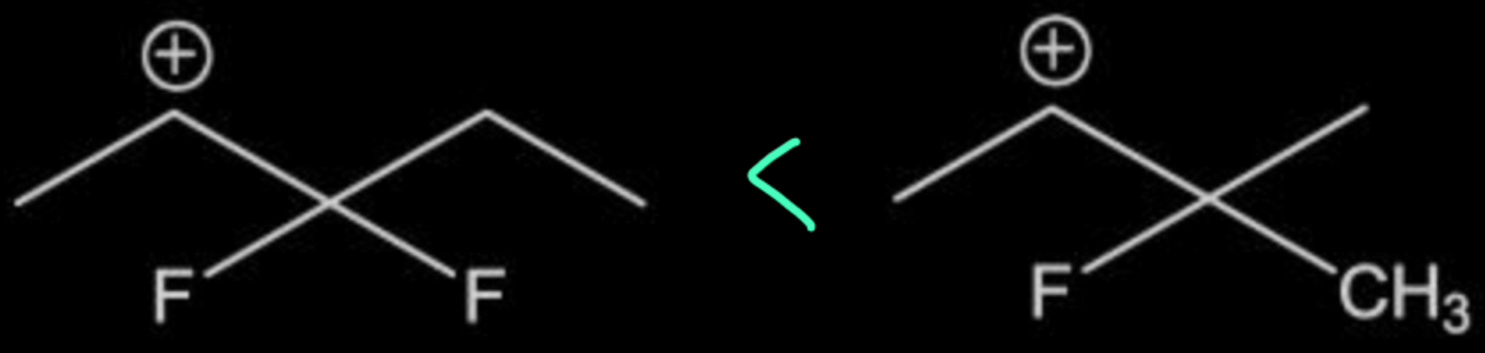
note → -ve charge → Stable → More EN

+ve charge → Stable → less EN

(a) $CH_3\overset{\oplus}{C}H_2$ (b) $CH_2(CD_3)-\overset{\oplus}{C}H_2$ (CD_3: +I) (c) $H_2C(NO_2)-\overset{\oplus}{C}H_2$ (NO_2: -I)

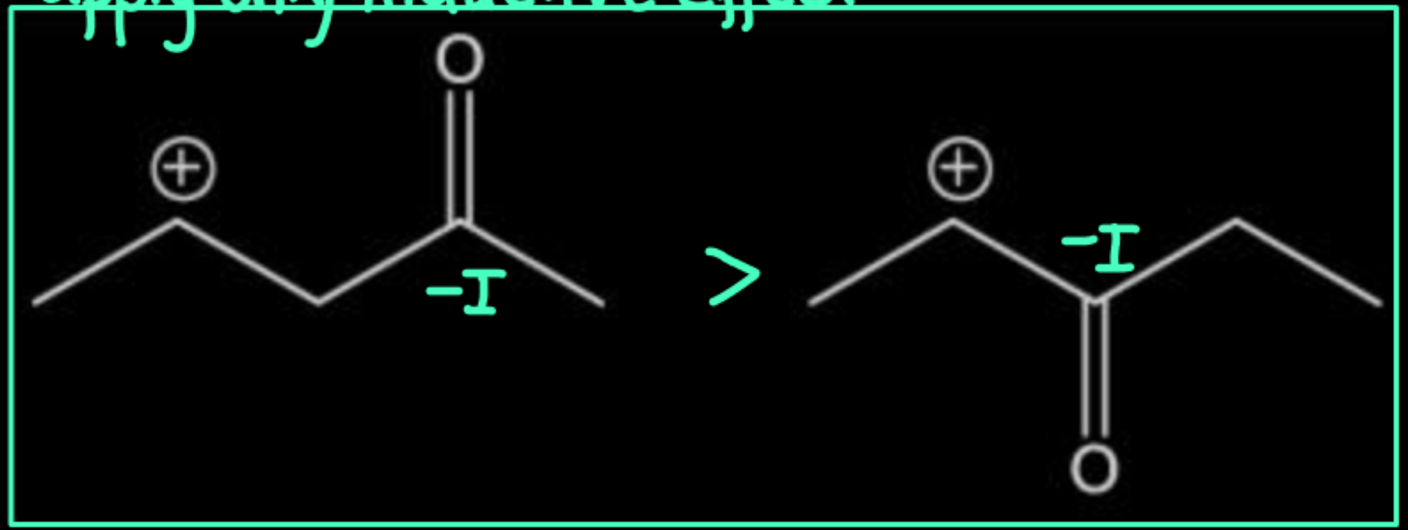
b > a > c

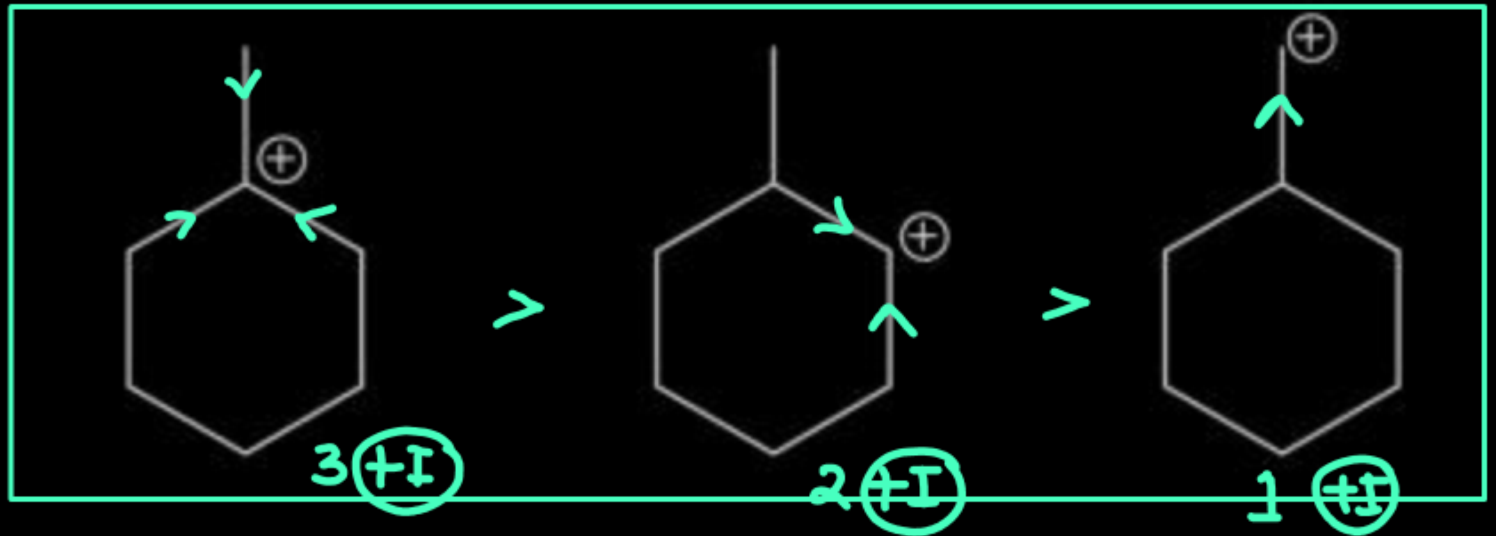


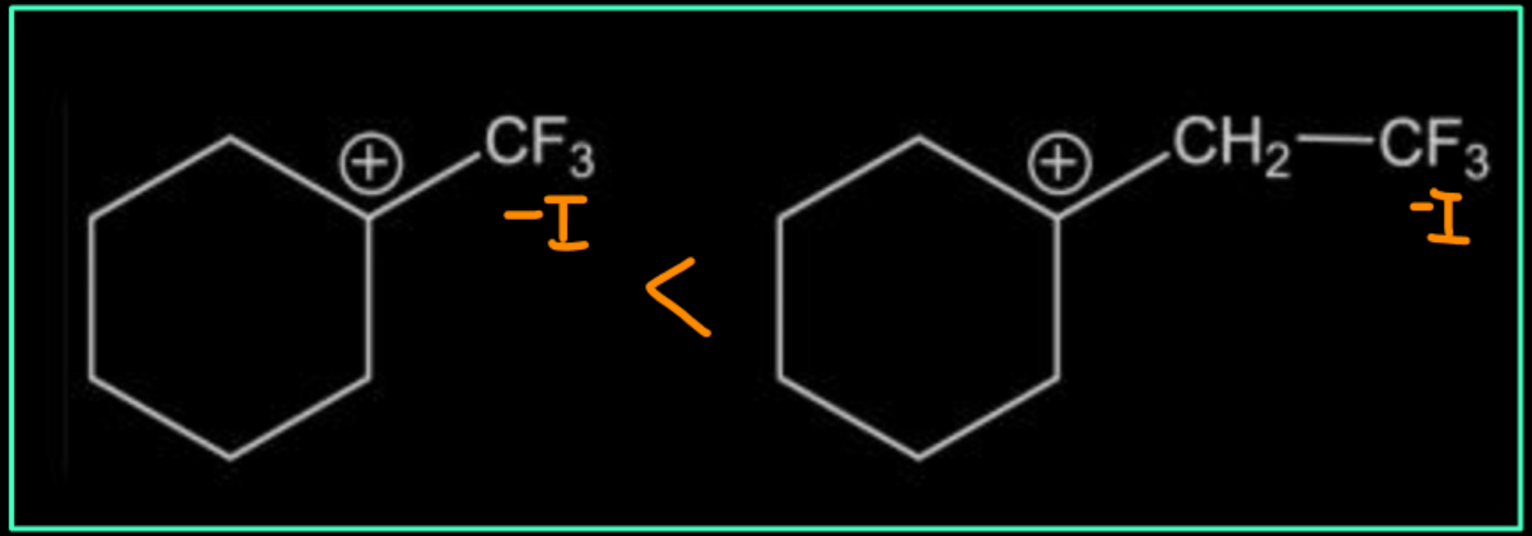


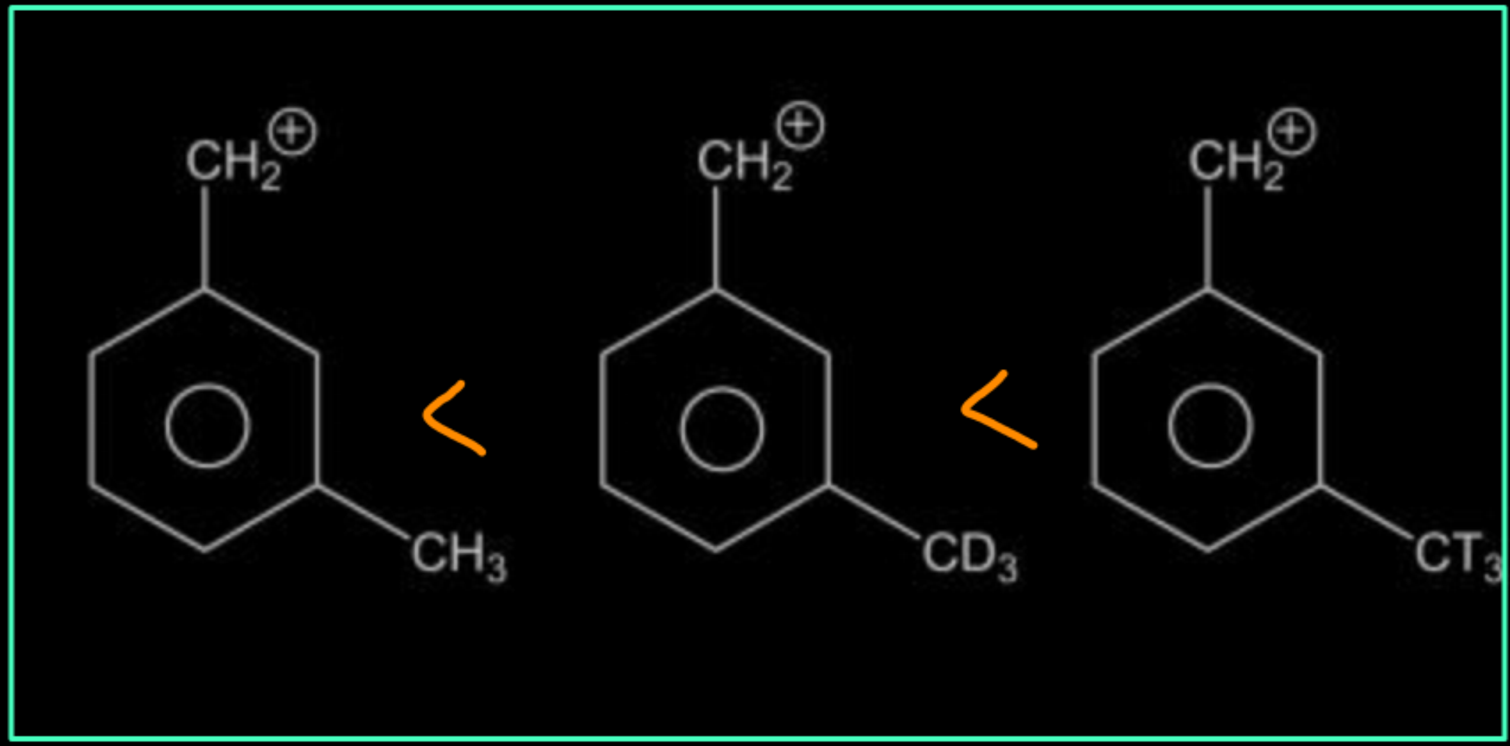
Ques. Which of the following carbocation is more stable?

apply only inductive effect









DNP- Rule

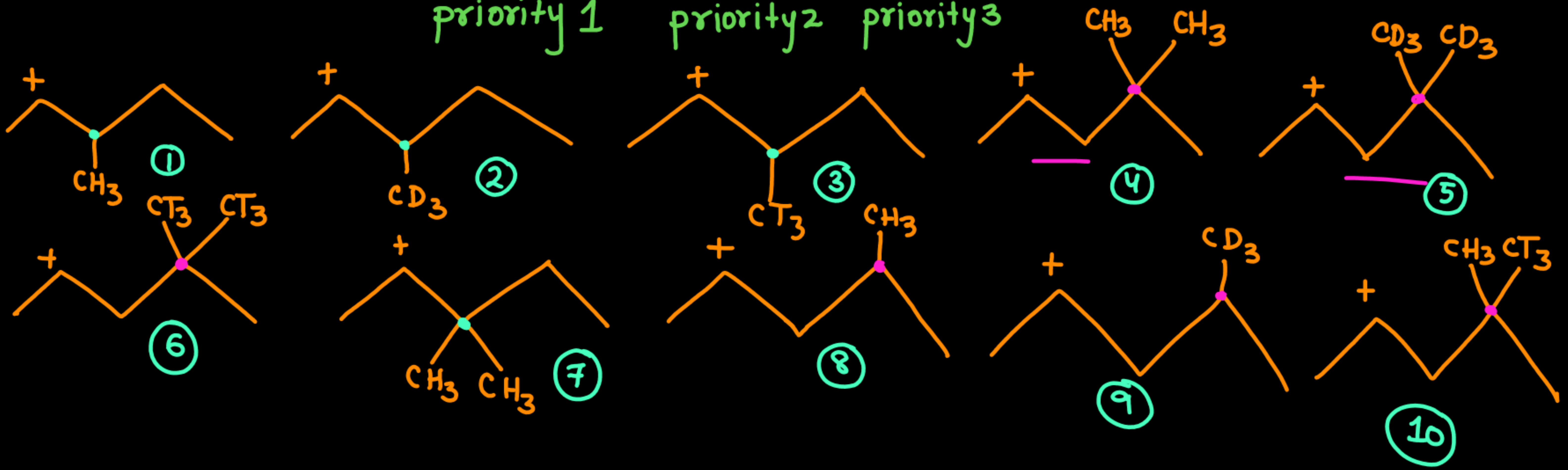
THANK YOU

All the Best!!

DNP- Rule

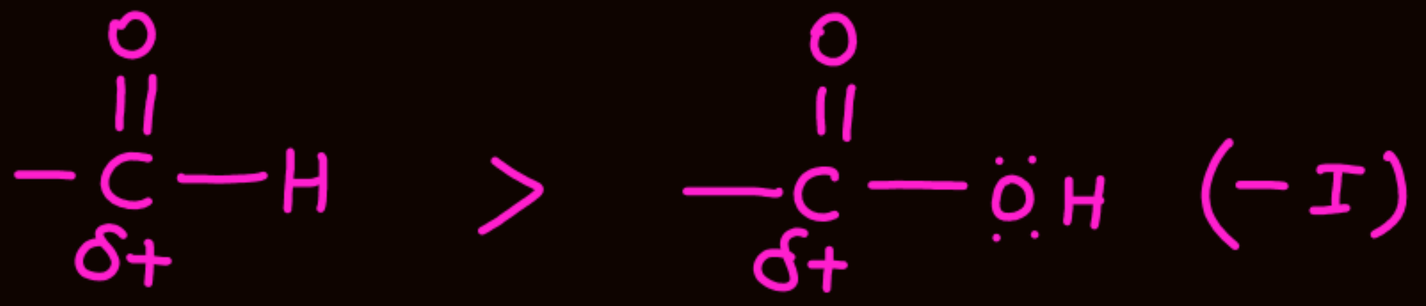
Distance Number Power Rule

priority 1 priority 2 priority 3



7 > 3 > 2 > 1 > 6 > 10 > 5 > 4 > 9 > 8

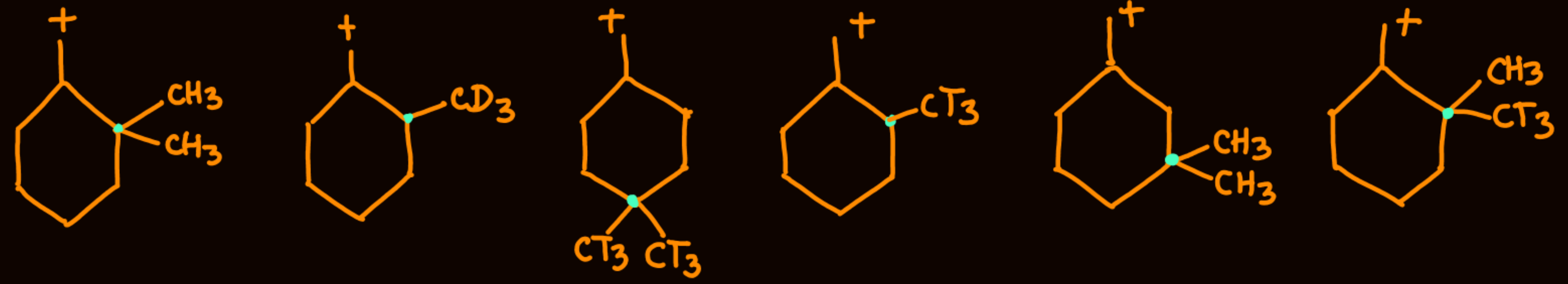
Q Why $-\overset{O}{\overset{\|}{C}}-H$ show more −I than $-\overset{O}{\overset{\|}{C}}-OH$??



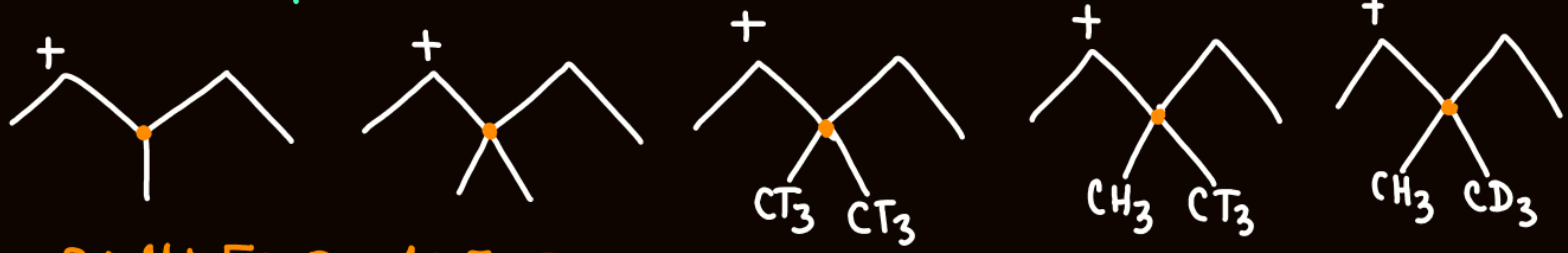
(δ+ is more)

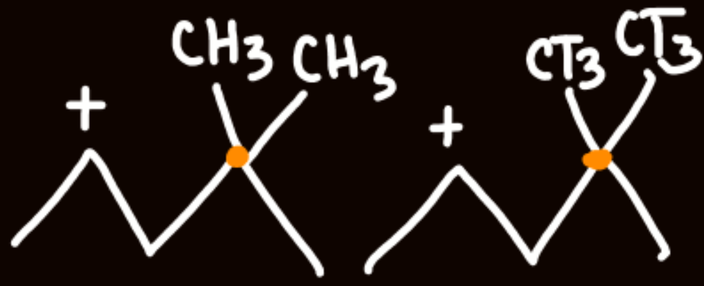
(δ+ is less)
oxy donates
lonepair.

Que

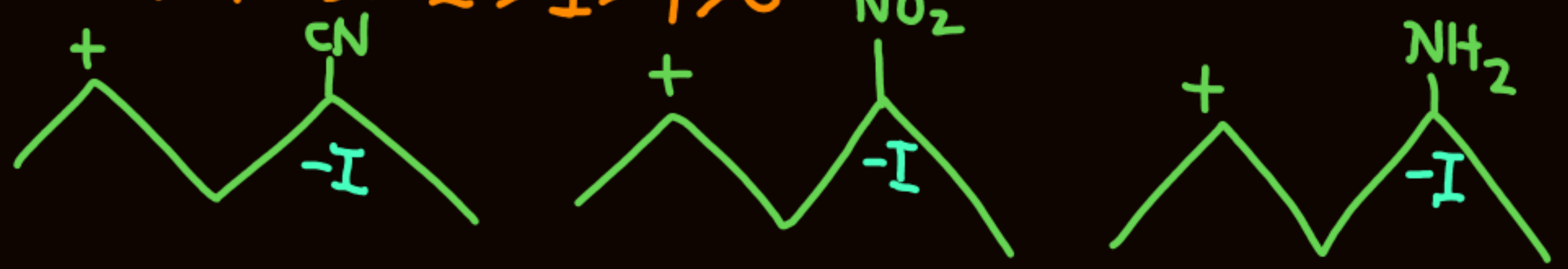


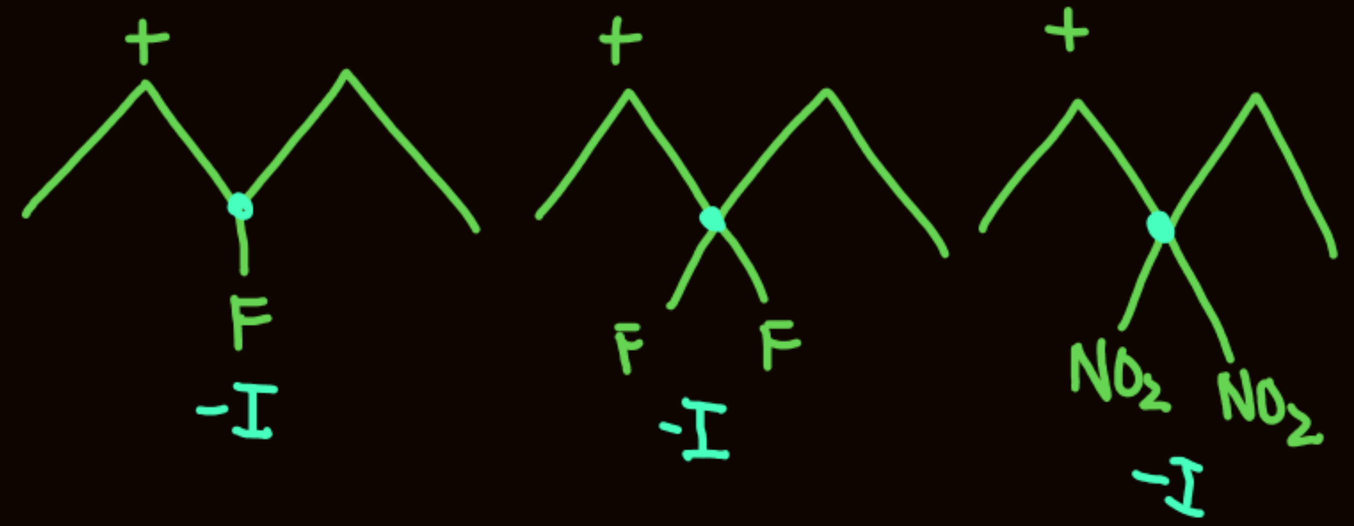
6 > 1 > 4 > 2 > 5 > 3



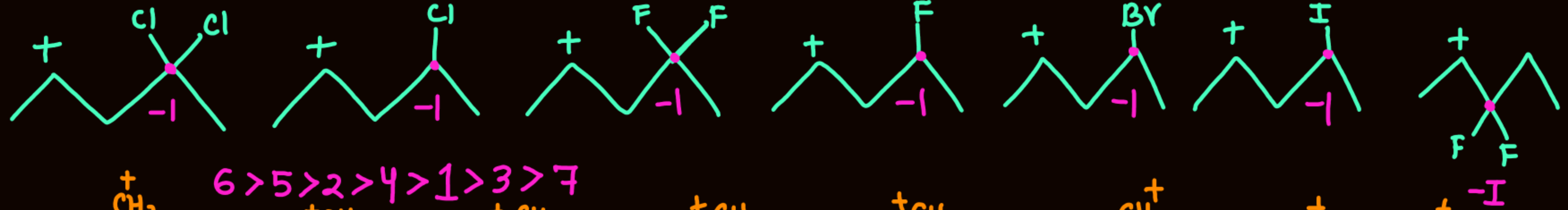


3 > 4 > 5 > 2 > 1 > 7 > 6



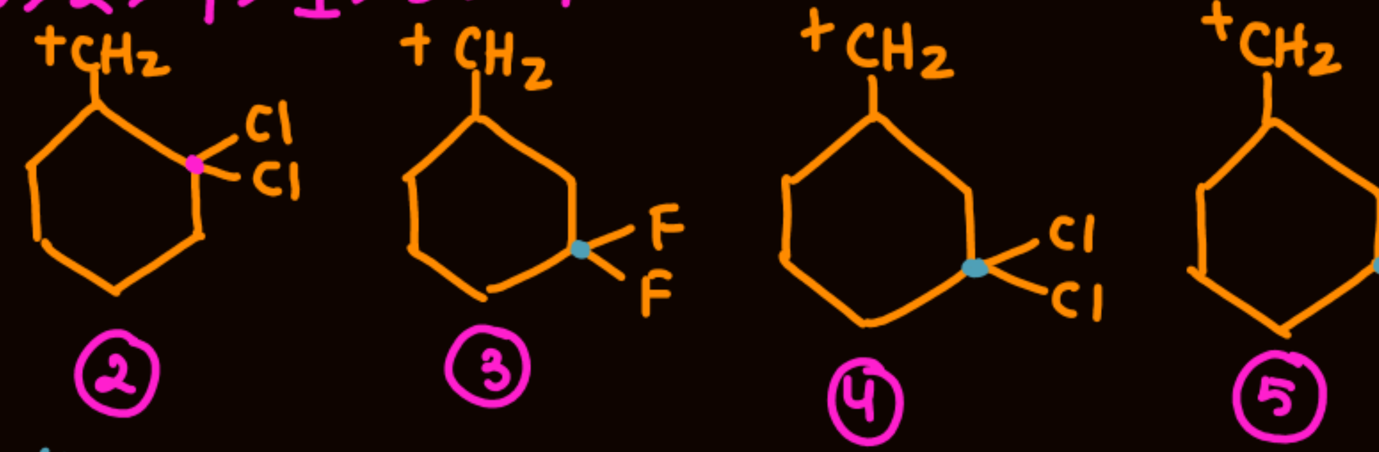


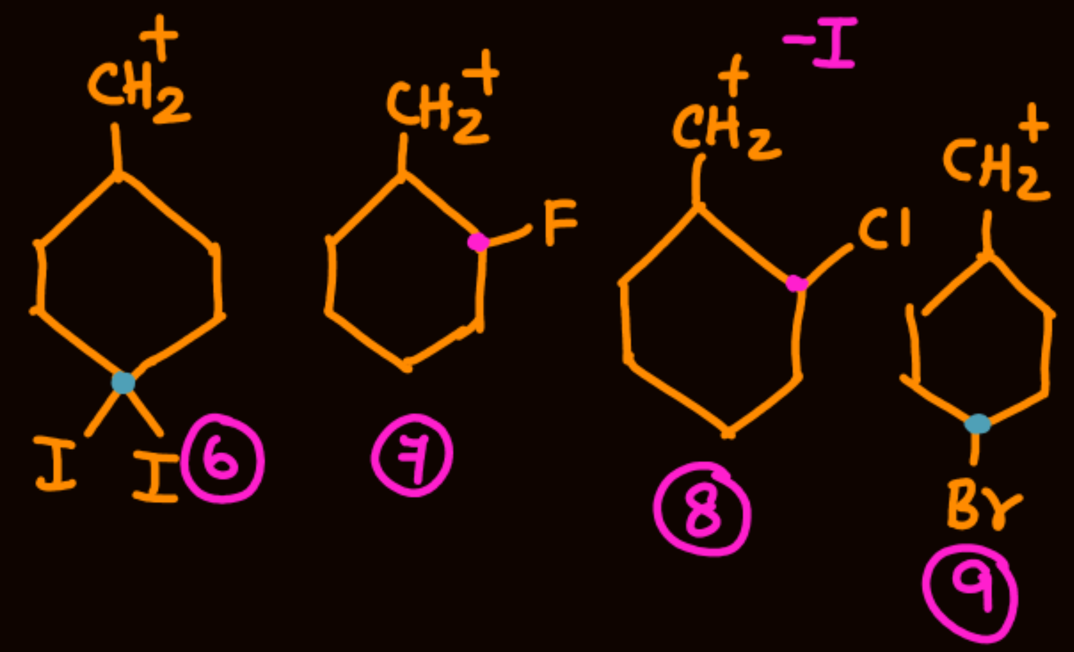
3 > 1 > 2 > 4 > 5 > 6



6 > 5 > 2 > 4 > 1 > 3 > 7







9 > 6 > 5 > 4 > 3 > 8 > 7 > 2 > 1

Stability of Carbanion

Stability of carbanion (CH_3^-) $\propto -I \propto \frac{1}{+I}$

ncert # For same period element → -ve charge → Stable on more EN atom.

ncert # For Same group element → -ve charge → Stable on Bigger Size.

Que Stability $CH_3^- < NH_2^- < OH^- < F^-$

Que Stability $F^- < Cl^- < Br^- < I^-$

Que Stability $O^{-2} < S^{-2} < Se^{-2} < Te^{-2}$

Que Stability $\overset{\ominus}{C}H_2-CH_3 < \overset{\ominus}{C}H=CH_2 < \overset{\ominus}{C}\equiv CH$

(sp^3 < sp^2 < sp)

Ques. Which of the following carbanion is more stable?

$$\underset{\underset{CH_3\ (+I)}{|}}{\overset{\overset{(+I)\ CH_3}{|}}{(+I)\ H_3C - C^{\ominus}}} < \underset{\underset{CH_3\ (+I)}{|}}{\overset{\ominus}{C}H} - CH_3\ (+I) < (+I)\ CH_3 - \overset{\ominus}{C}H_2 < \overset{\ominus}{C}H_3$$

$$H_2\overset{\ominus}{C} - \underset{\underset{F}{|}}{CH} - CH_2 - CH_3 > H_2\overset{\ominus}{C} - CH_2 - \underset{\underset{F}{|}}{CH} - CH_3 > H_2\overset{\ominus}{C} - CH_2 - CH_2 - CH_2 - F$$

$$F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$$

Period ———— group

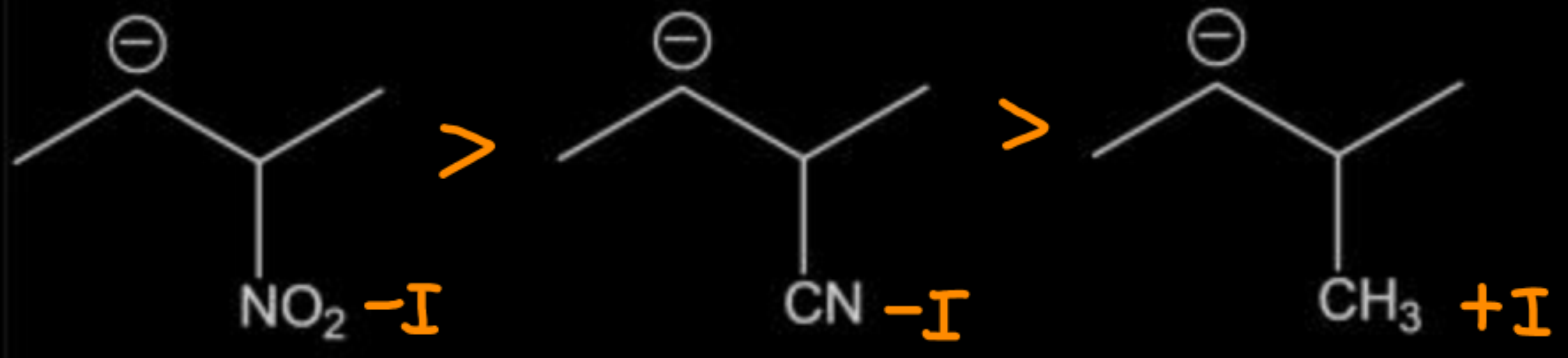
* $HC \equiv C^{\ominus}$ (sp C, 3.25) $\quad NH_2^{\ominus}$ (sp^3 N, 3.0) $\quad OH^{\ominus}$ (3.5) $\quad SH^{\ominus}$

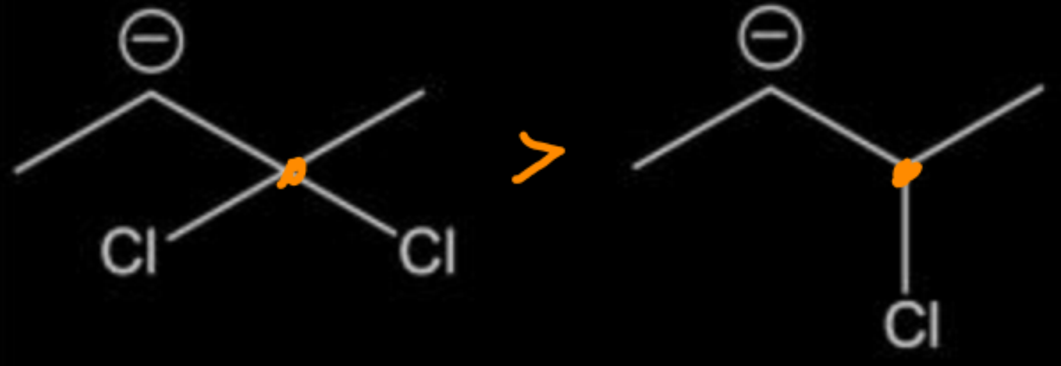
$$\overset{-}{S}H > O\overset{-}{H} > \overset{-}{C} \equiv CH > \overset{-}{N}H_2$$

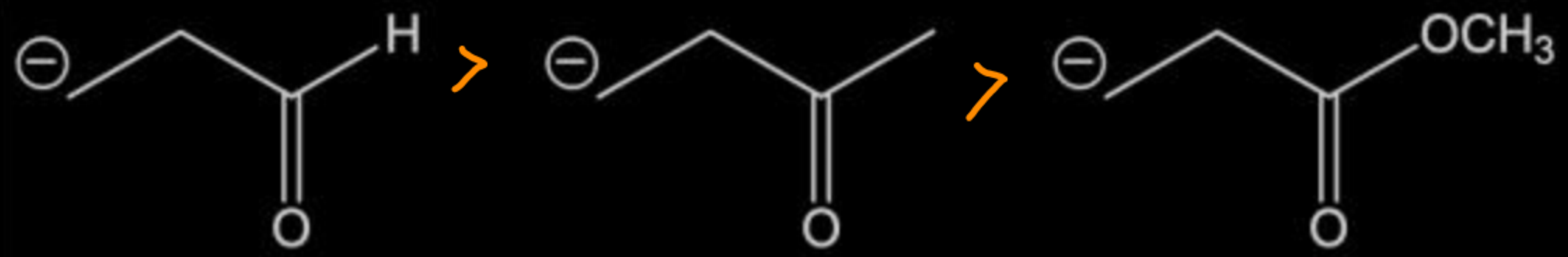
$$4 > 3 > 1 > 2$$

Ques. Which of the following carbanion is more stable?

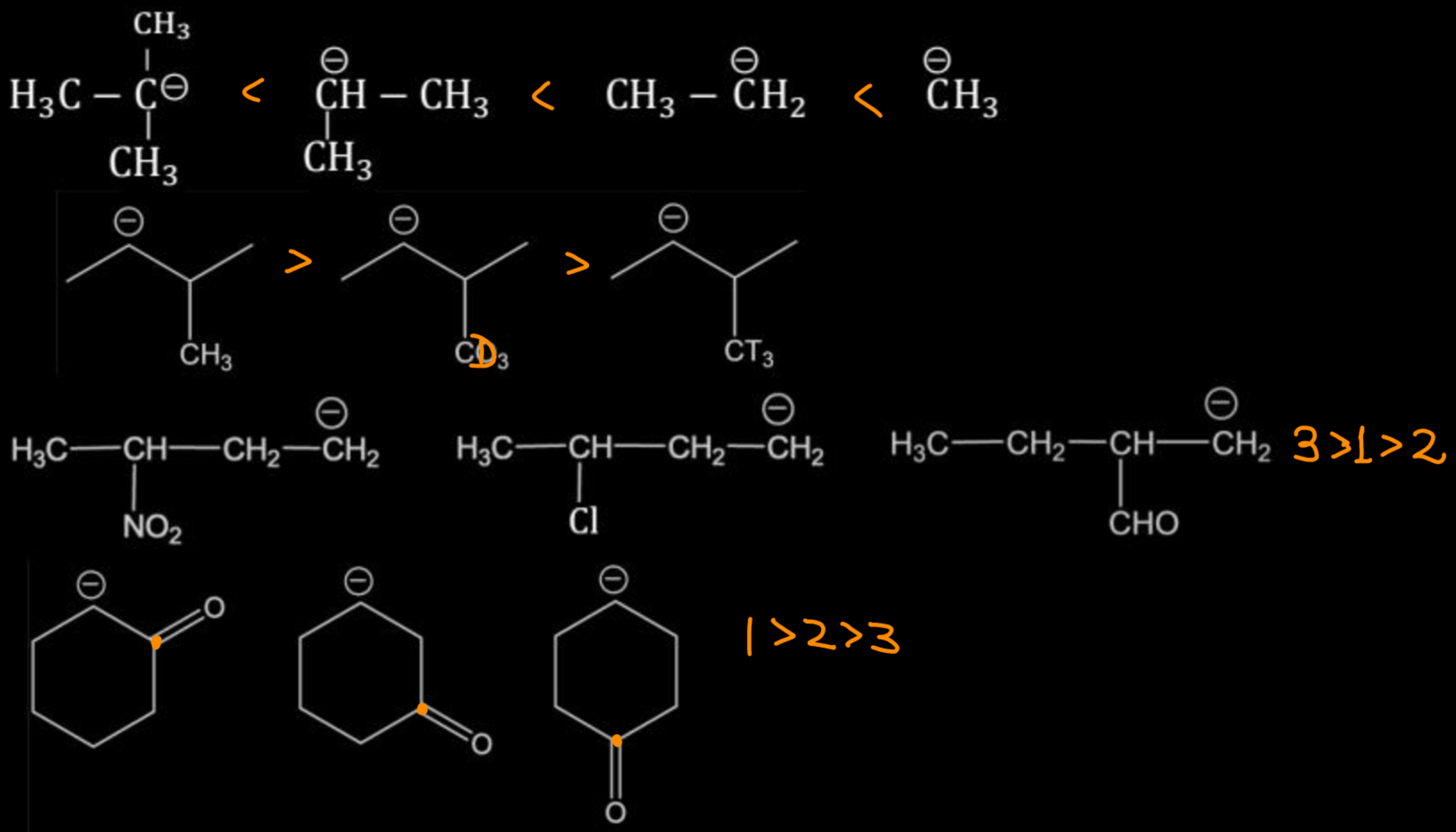
$$H_2\overset{\ominus}{C} - \underset{\displaystyle F}{\underset{|}{CH}} - CH_2 - CH_3 > H_2\overset{\ominus}{C} - CH_2 - \underset{\displaystyle F}{\underset{|}{CH}} - CH_3 > H_2\overset{\ominus}{C} - CH_2 - CH_2 - CH_2 - F$$



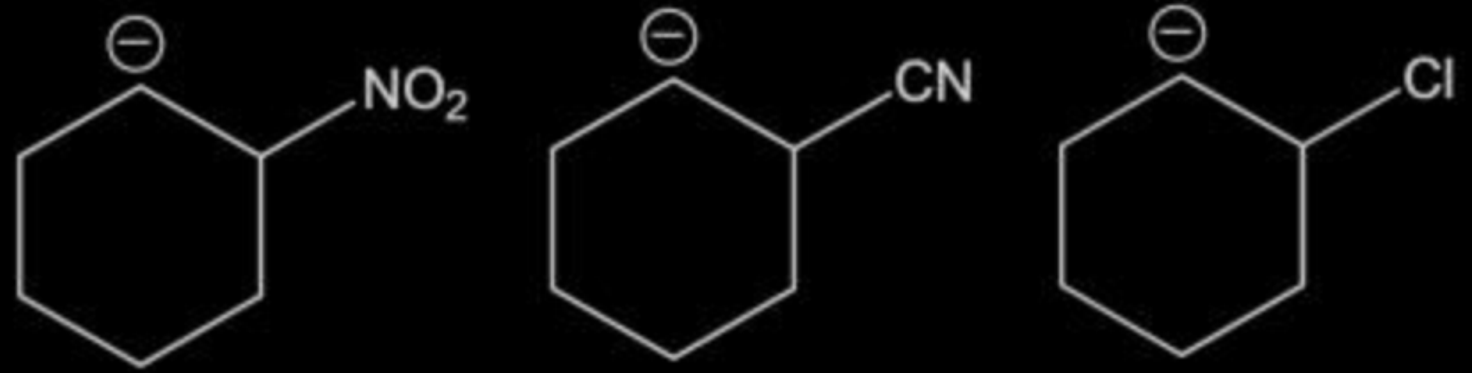




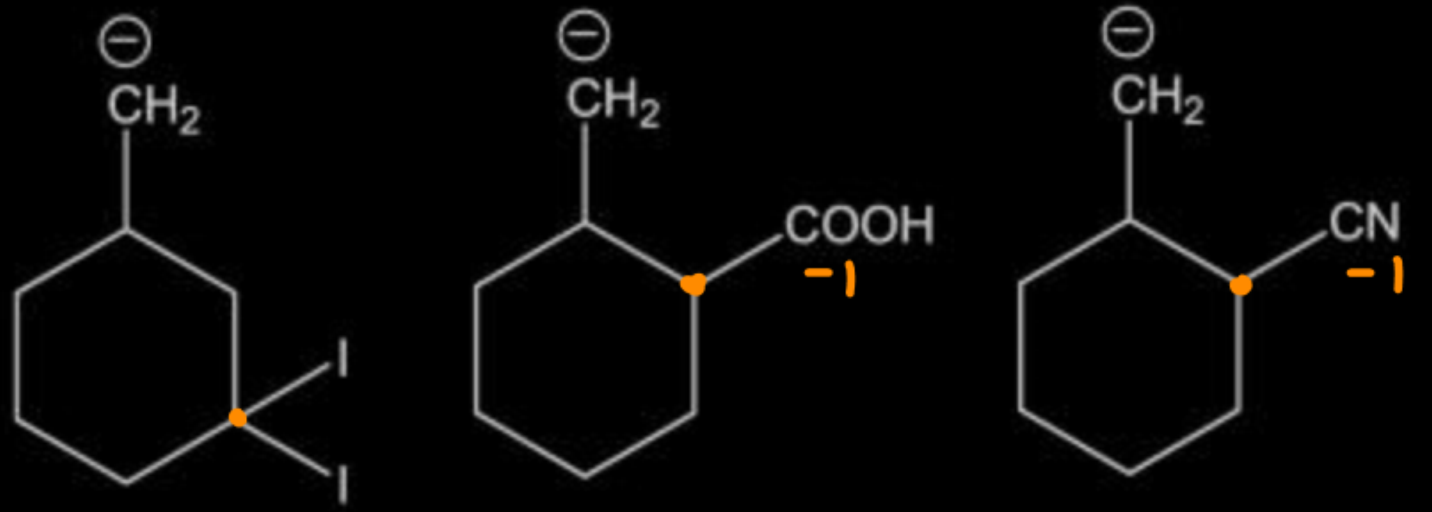
Ques. Which of the following carbanion is more stable?



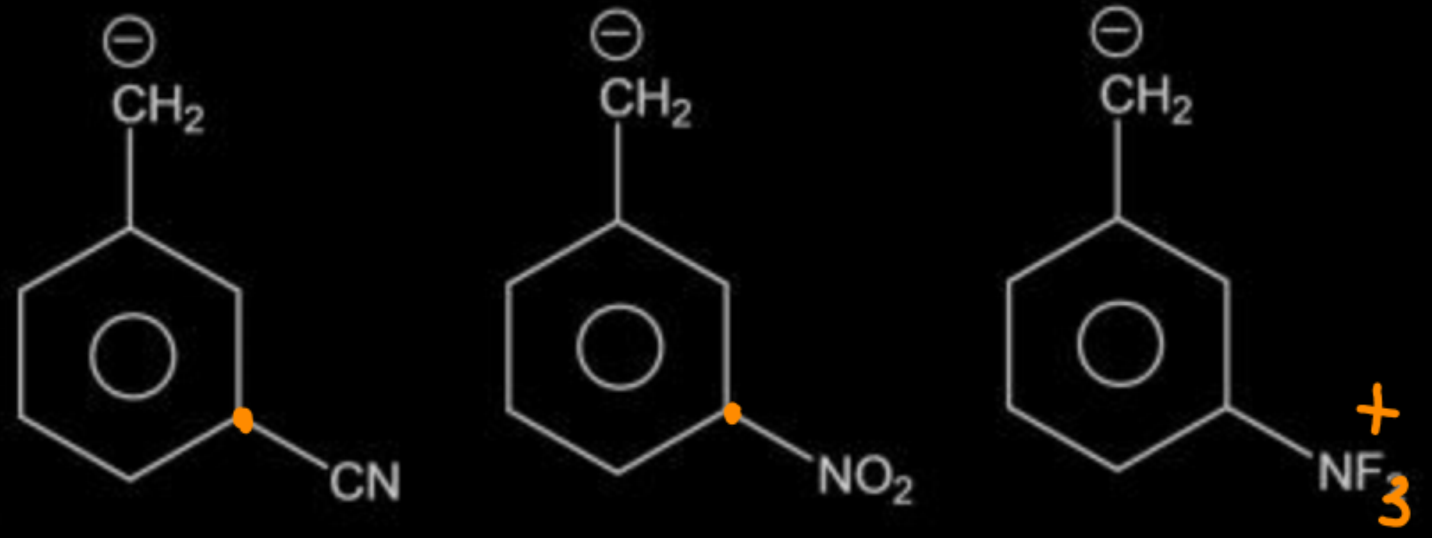
Ques. Which of the following carbanion is more stable?



1 > 2 > 3

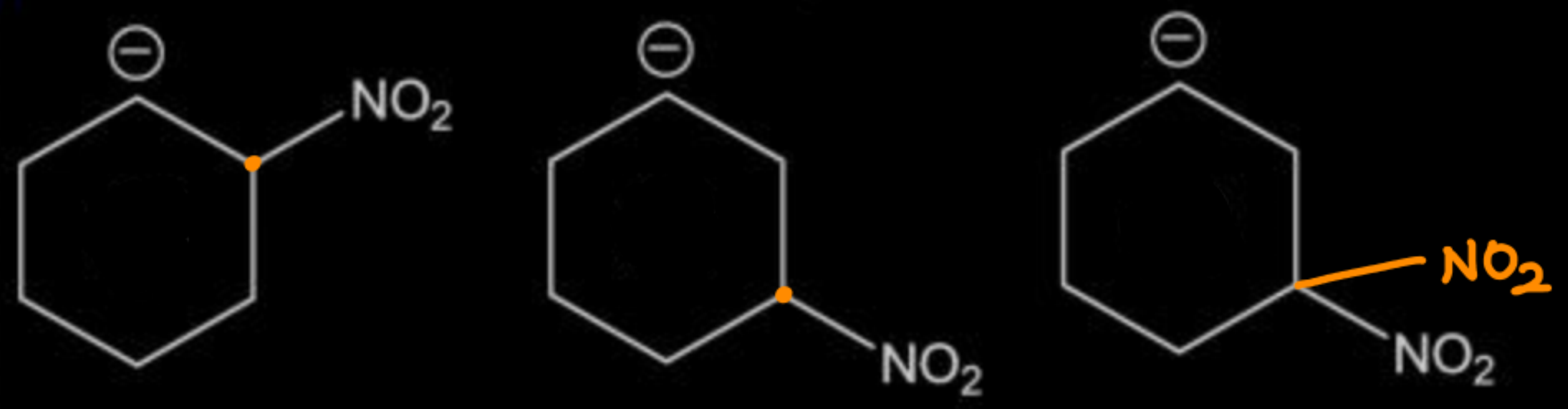


3>2>1

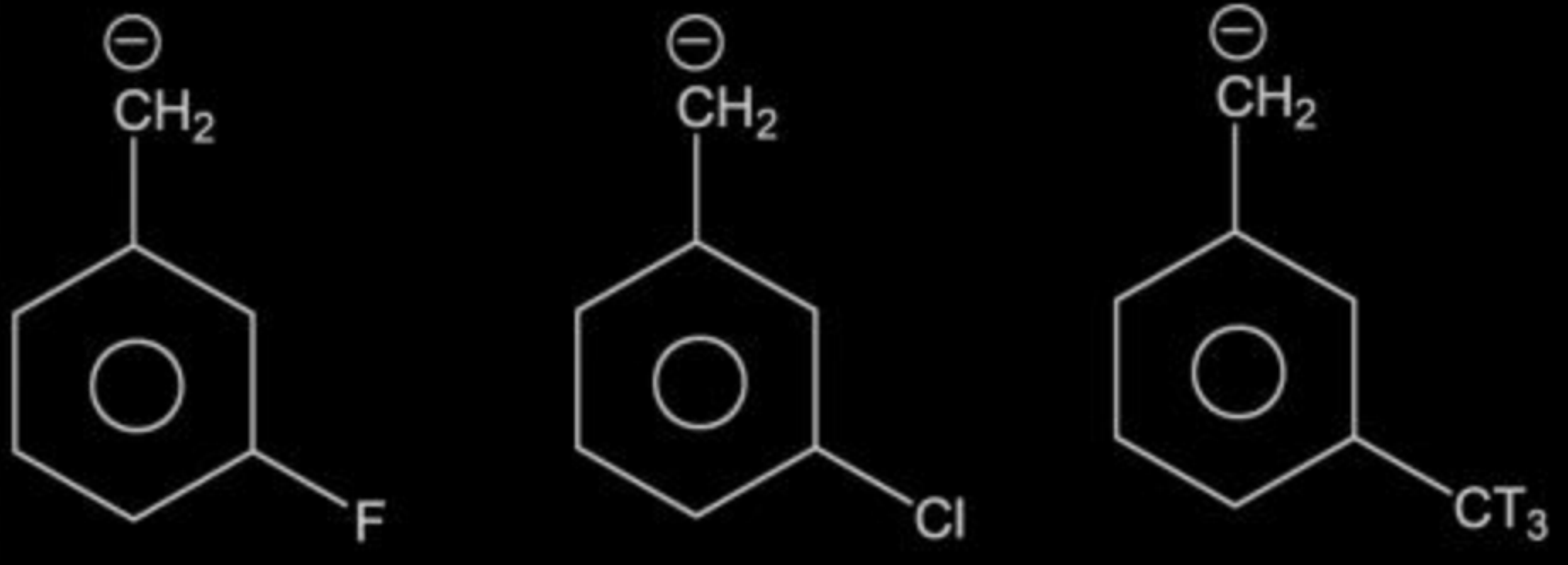


3>2>1

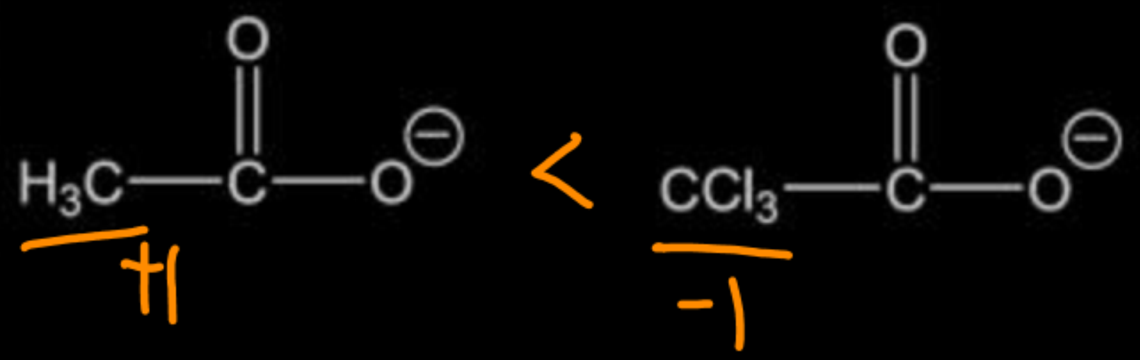
Ques. Which of the following carbanion is more stable?



1 > 3 > 2



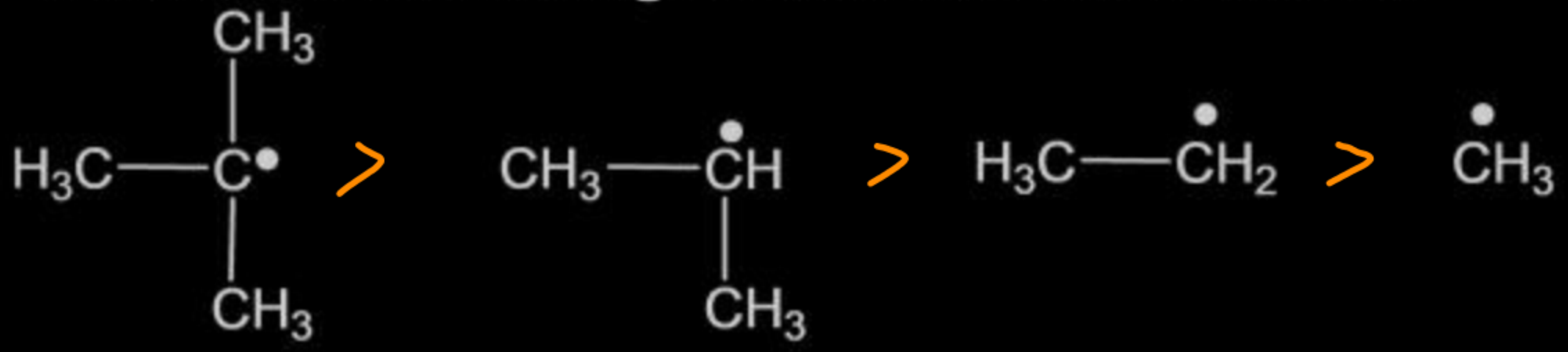
1>2>3



Stability of Carbon Free Radical

Stability of Carbon Free Radical $\propto +I \propto \frac{1}{-I}$

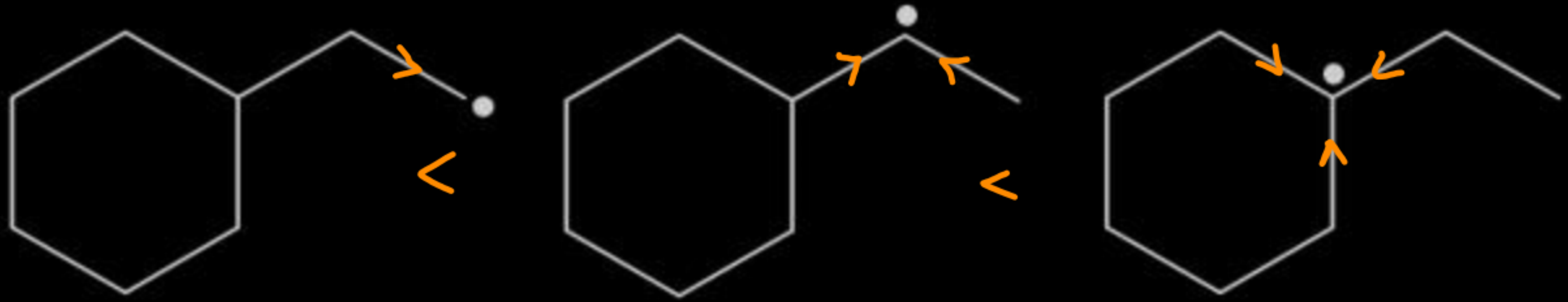
Ques. Which of the following free radical is more stable?

1. 

2. 

3. 

4. 

5. 

15 Jan — 31 Jan

THANK YOU
All the Best!!

Career Point

20 June - 2019

Life Lec 1

6-8am

8·30 – 3·00

4·00 – 6·00

7·00 – 9·00

10 – 12

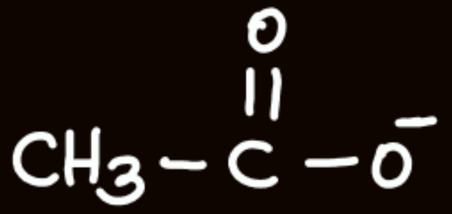
B

15 days only

6hr → Selection

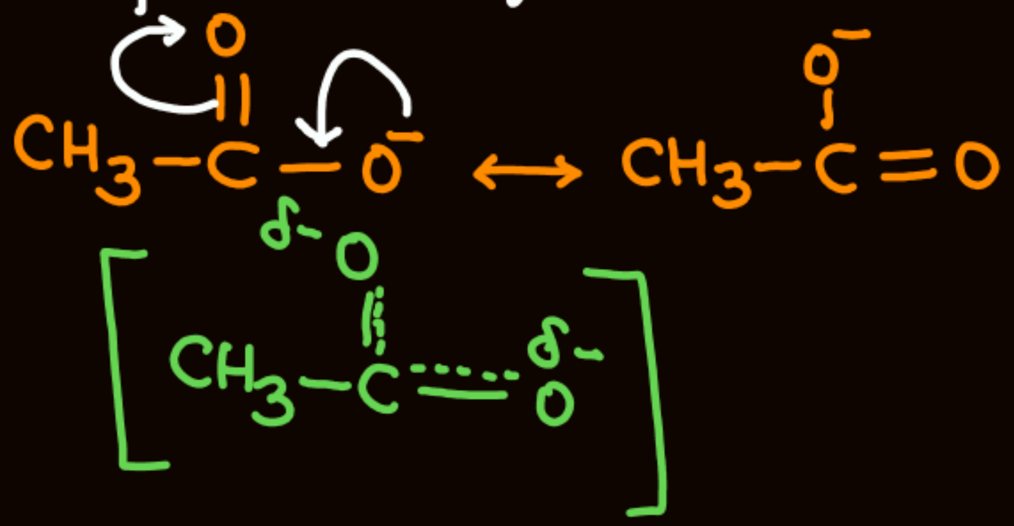
Resonance

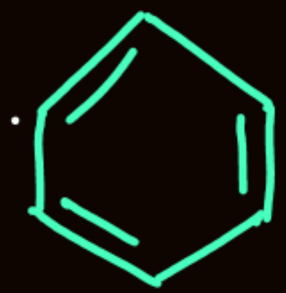
1.0 + 2.0



C = O, C — O } Theoretically 2 different type of Bond.

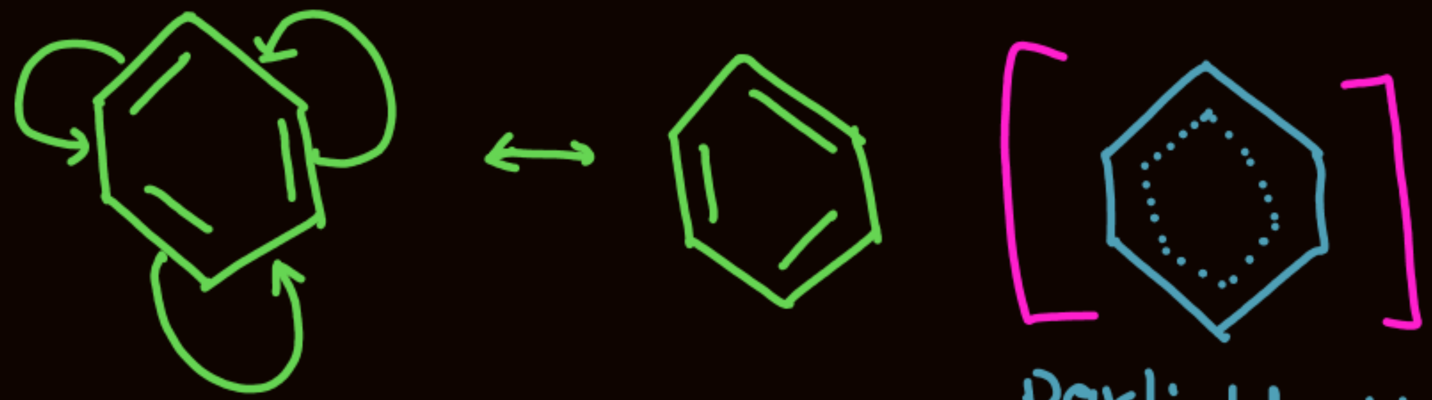
But experimentally, all C—O bonds are same.





C = C, C — C } Theoretically, 2 different type of Bond

But experimentally, all C–C bonds are same.



C–C Single bond = 1.54 A°

C=C double bond = 1.34 A°

Benzene → C–C bond length = 1.39 A°
(partial double bond)

Resonance

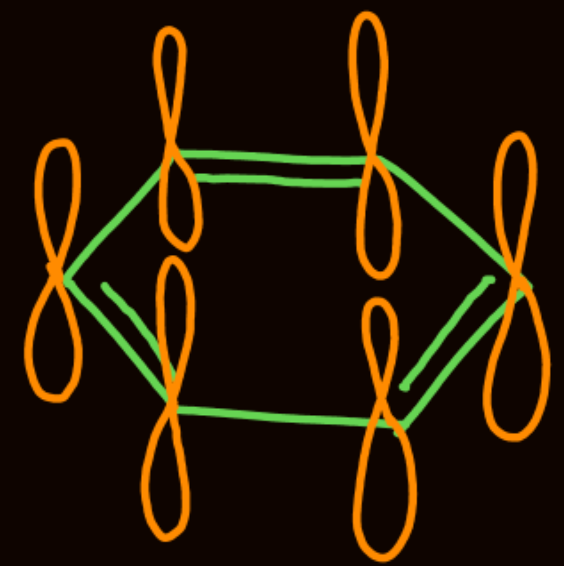
- Delocalization of Pi electron from one bond to other in a comp is called Resonance.
- Complete delocalisation.
- parmanent effect.

7 Condition of Reso

1. $CH_2=CH-\overset{\oplus}{C}H_2$ — $\pi\ \sigma\ \oplus$
2. $CH_2=CH-\overset{\ominus}{C}H_2$ — $\pi\ \sigma\ \ominus$
3. $CH_2=CH-\ddot{C}H_2$ — $\pi\ \sigma$ (:)
4. $CH_2=CH-\dot{C}H_2$ — $\pi\ \sigma$ (·)
5. $CH_2=CH-CH=CH_2$ — $\pi\ \sigma\ \pi$
6. $p\pi-p\pi$ Resonance — $\overset{\oplus}{C}H_2-\ddot{O}-H$ $\overset{+}{C}H_2-\ddot{Cl}:$
7. $p\pi-d\pi$ Resonance — $\overset{\ominus}{C}H_2-\ddot{Cl}:$ $\overset{-}{C}H_2-\ddot{S}H$

10 Important Points of Reso

1. Resonating structures are separated by double arrow. (⟷) (⇌)
2. In Resonance, position of atom donot change, Sigma bond donot change, only position of pi bond/pi electron changes.
3. In Resonance, num of electron do not change (paired electron/Unpaired electron)
4. In Resonance, atoms must be planar (sp/sp^2)
5. In Resonance, p orbitals of atoms must be parallel.



6. Resonance & Resonating Str is Hypothetical Concept.
7. Resonance Hybrid is a real structure.
8. Resonance Hybrid is most stable structure among all Resonating Str.
9. Resonance Hybrid is combination of all Resonating Str.
10. Most Stable Resonating Str contributes maximum to Resonance Hybrid.
11. In Resonance, Complete charge remains same.

Drawing of Resonating Structures

① $\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2^{\oplus} \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH_2 \cong \left[\overset{\delta+}{C}H_2 \cdots CH \cdots \overset{\delta+}{C}H_2\right] \Rightarrow$ 2RS

Trick → charge → 1

doublebond → 2,3

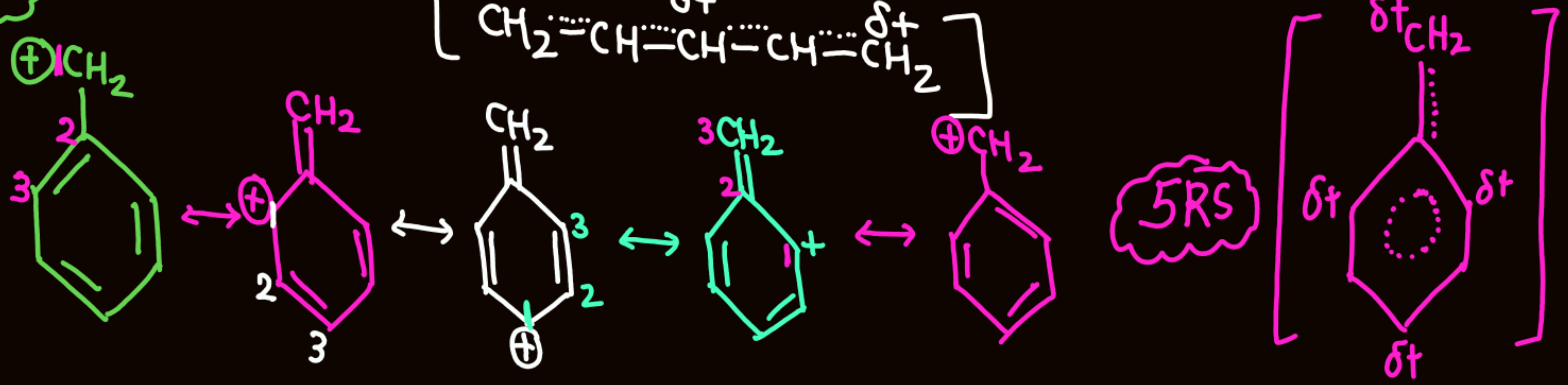
2,3 का bond 1,2 में transfer 1 का charge 3 में transfer

② $CH_2=CH-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_2^{\oplus} \longleftrightarrow \overset{3}{C}H_2=\overset{2}{C}H-\overset{\oplus}{\overset{1}{C}H}-CH=CH_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH-CH=CH_2$

3RS

$\left[\overset{\delta+}{C}H_2 \cdots CH \cdots \overset{\delta+}{C}H \cdots CH \cdots \overset{\delta+}{C}H_2\right]$

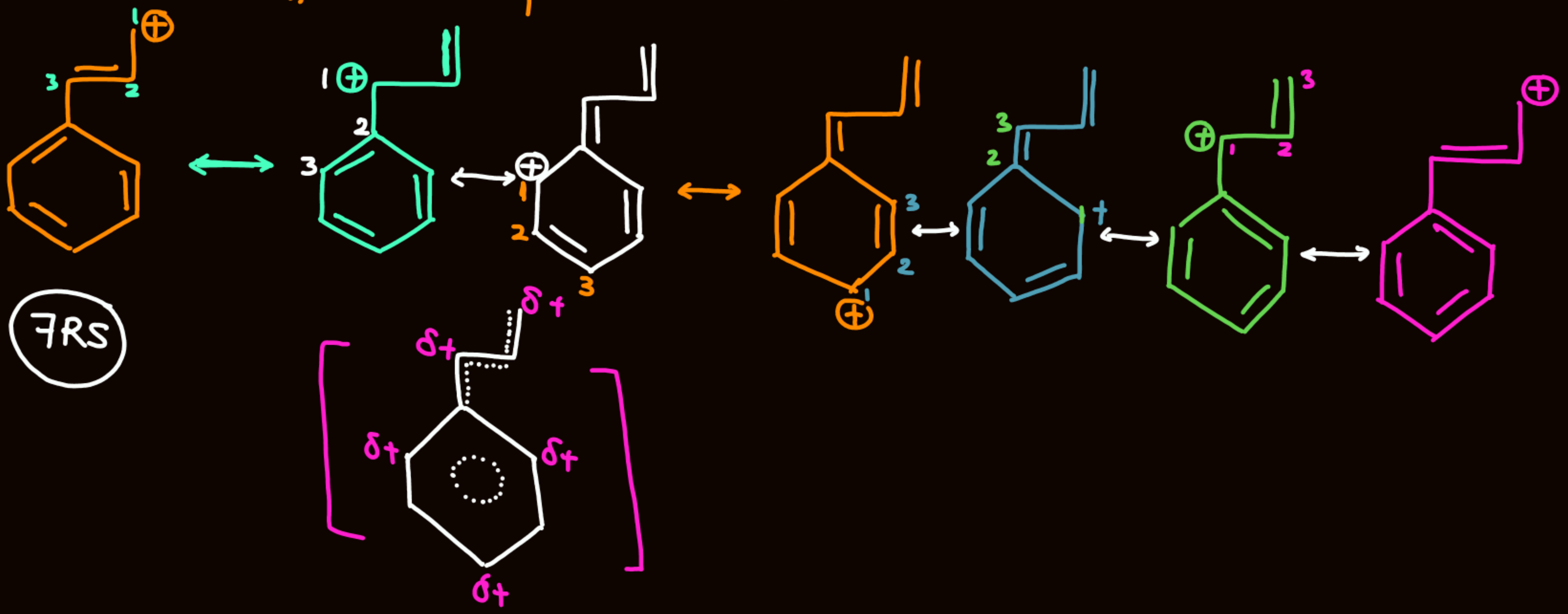
③



Note → Resonance effect operates only on ortho & para in Benzene.

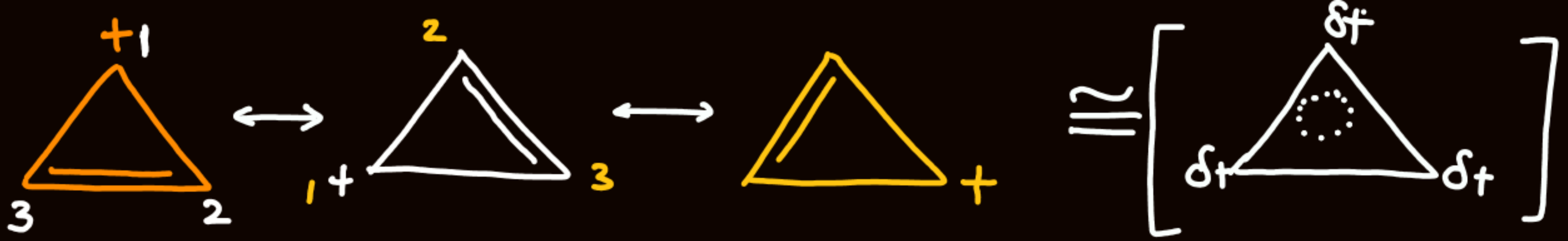
Resonance effect cannot operate on meta.

Q4



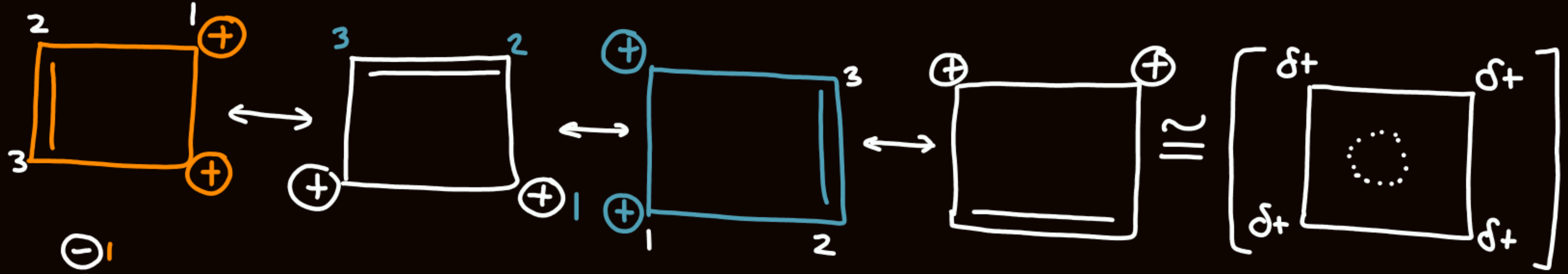
7RS

Q5
3RS

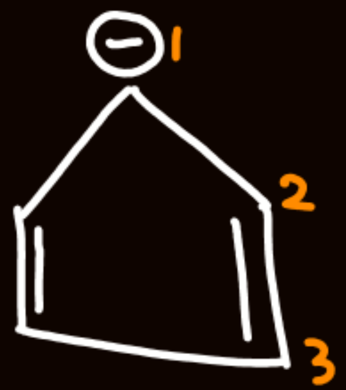


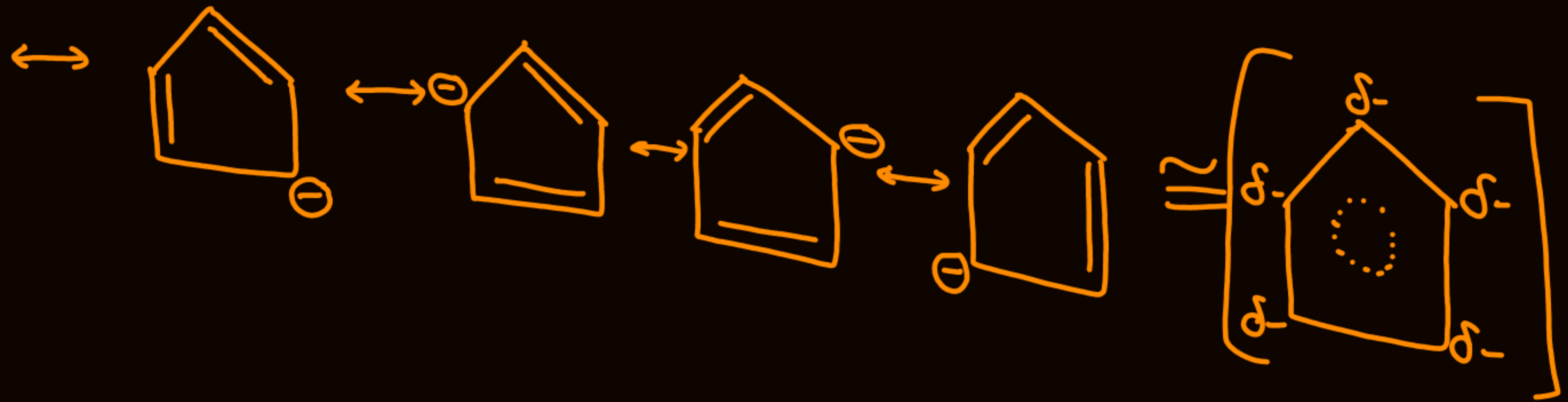
3RS

Q6
4RS



Q7

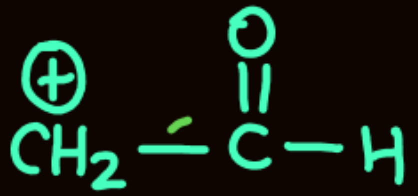




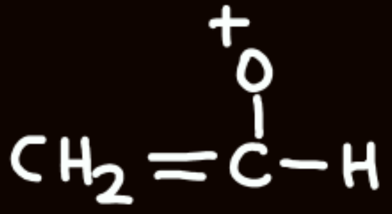
HW
Q8
5Rs



Q9

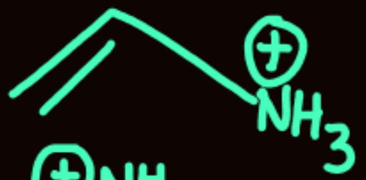


(no Resonance)



(unstable) [More En oxygen Can not donate its pi bond]

Q10



(no Resonance)

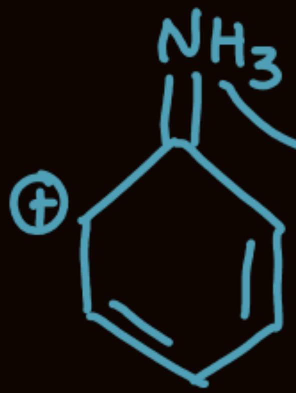


→ nitrogen Cannot form 5 bonds.

Q11



(no Resonance)
(only Resonance in Benzene)



Q12





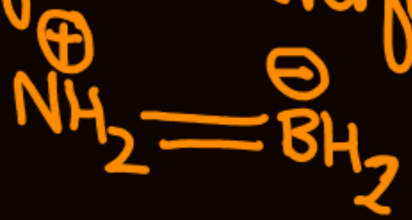
(no Resonance)

↓ Boron, nitrogen can never form 5 bond.

Q13



↔



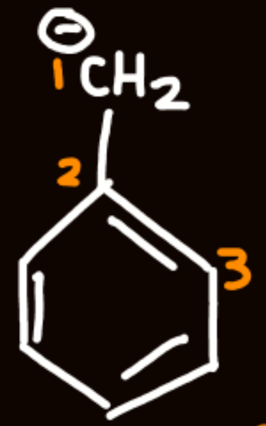
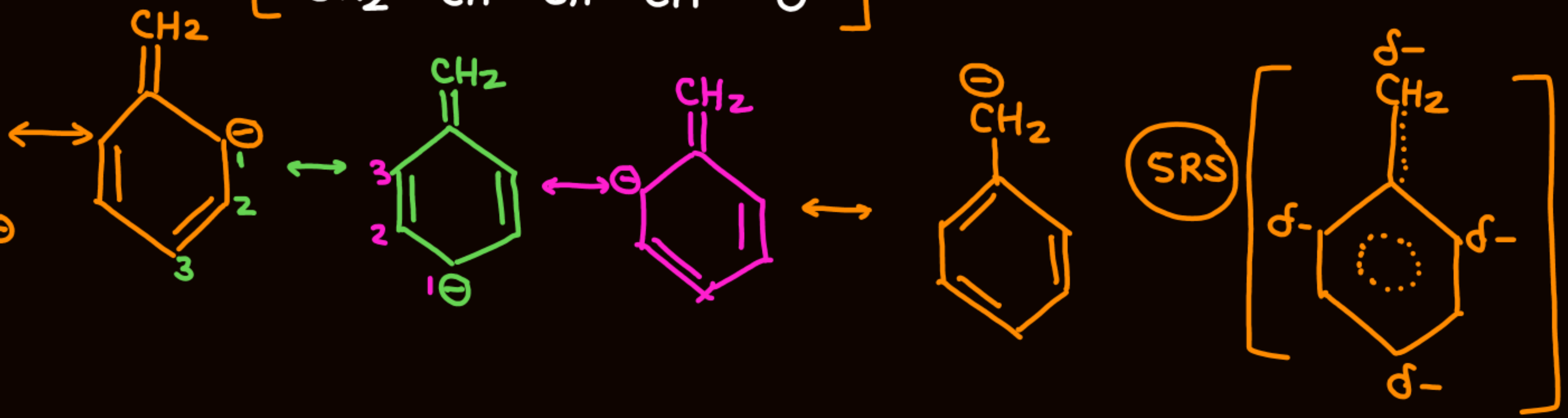
(it shows Resonance → pπ-pπ Resonance)

Que $\overset{3}{CH_2}=\overset{2}{CH}-\overset{\ominus}{\underset{1}{CH_2}} \longleftrightarrow \overset{\ominus}{CH_2}-CH=CH_2 \cong \left[\overset{\delta-}{CH_2}\cdots CH \cdots \overset{\delta-}{CH_2}\right]$

Que $CH_2=CH-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{\overset{-}{O}} \longleftrightarrow \underset{3}{CH_2}=\underset{2}{CH}-\overset{\ominus}{\underset{1}{CH}}-CH=O \longleftrightarrow \overset{\ominus}{CH_2}-CH=CH-CH=O$

$\left[\overset{\delta-}{CH_2}\cdots CH \cdots \overset{\delta-}{CH}\cdots CH \cdots \overset{\delta-}{O}\right]$

Que

HW **Que** FRS

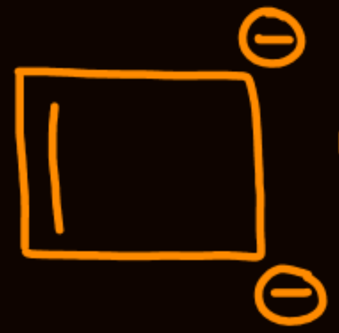


HW Que



3Rs

HW Que



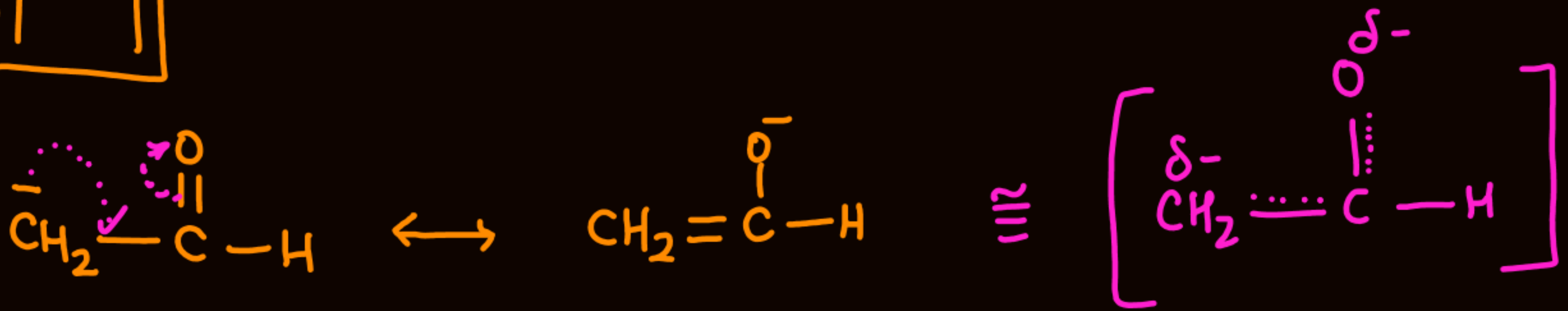
4Rs

HW Que



5Rs

Que



Resonating Structures & Resonance Hybrid

2RS

Q1 $CH_2=CH-\ddot{N}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{N}H_2 \cong \left[\overset{\delta-}{C}H_2 \cdots CH \cdots \overset{\delta+}{N}H_2\right]$

3RS

Q2 $CH_2=CH-CH=CH-\ddot{O}H \longleftrightarrow \underset{3}{CH_2}=\underset{2}{CH}-\underset{1}{\overset{\ominus}{C}H}-CH=\overset{\oplus}{O}H \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH-CH=\overset{\oplus}{O}H$

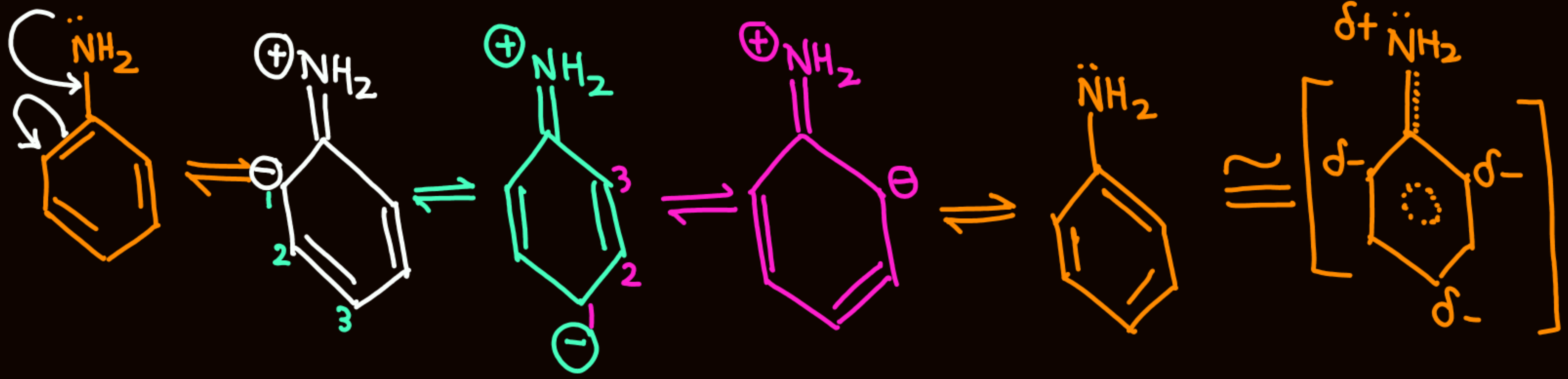
$\cong \left[\overset{\delta-}{C}H_2 \cdots CH \cdots \overset{\delta-}{C}H \cdots CH \cdots \overset{\delta+}{O}H\right]$

2RS

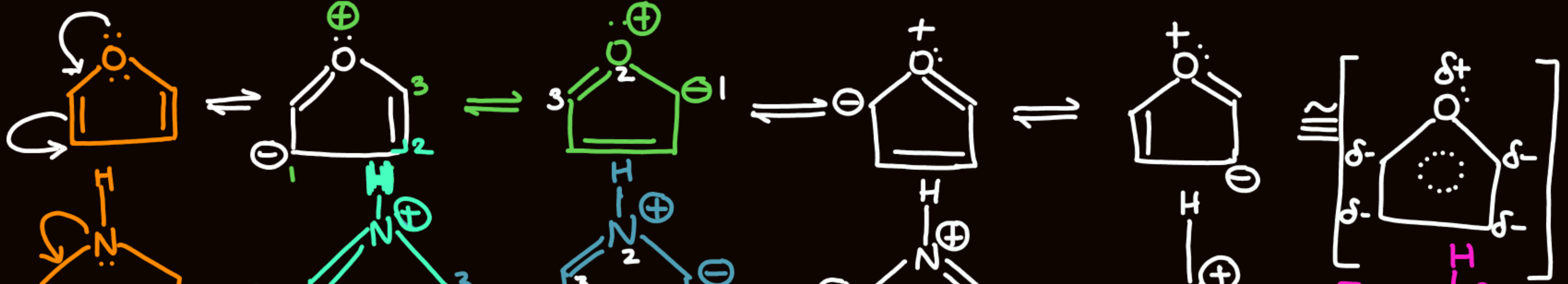
Q3 $H\ddot{O}-CH=CH-\ddot{N}H_2 \longleftrightarrow H\ddot{O}-H\overset{\ominus}{C}-HC=\overset{\oplus}{N}H_2 \cong \left[HO-\overset{\delta-}{C}H \cdots CH \cdots \overset{\delta+}{N}H_2\right]$

More EN (O) — less EN (N)

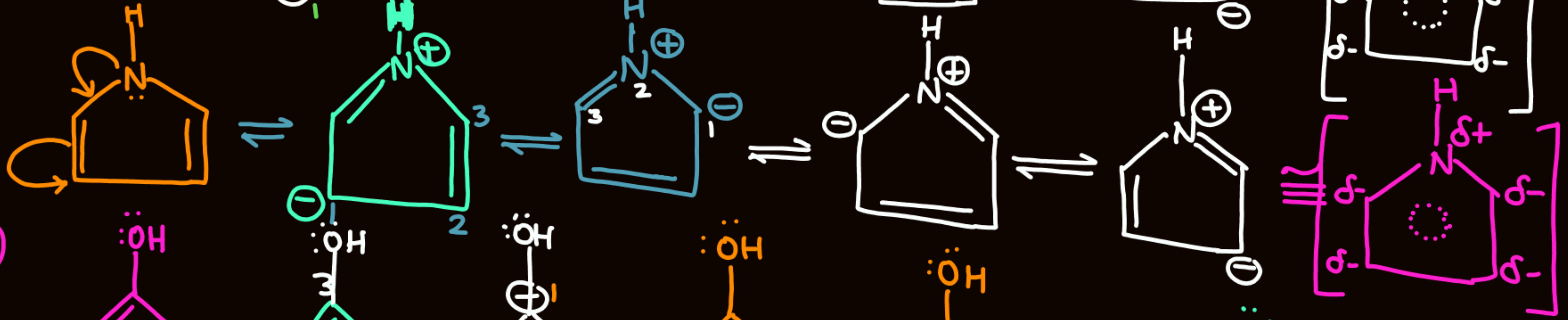
Q4 5RS



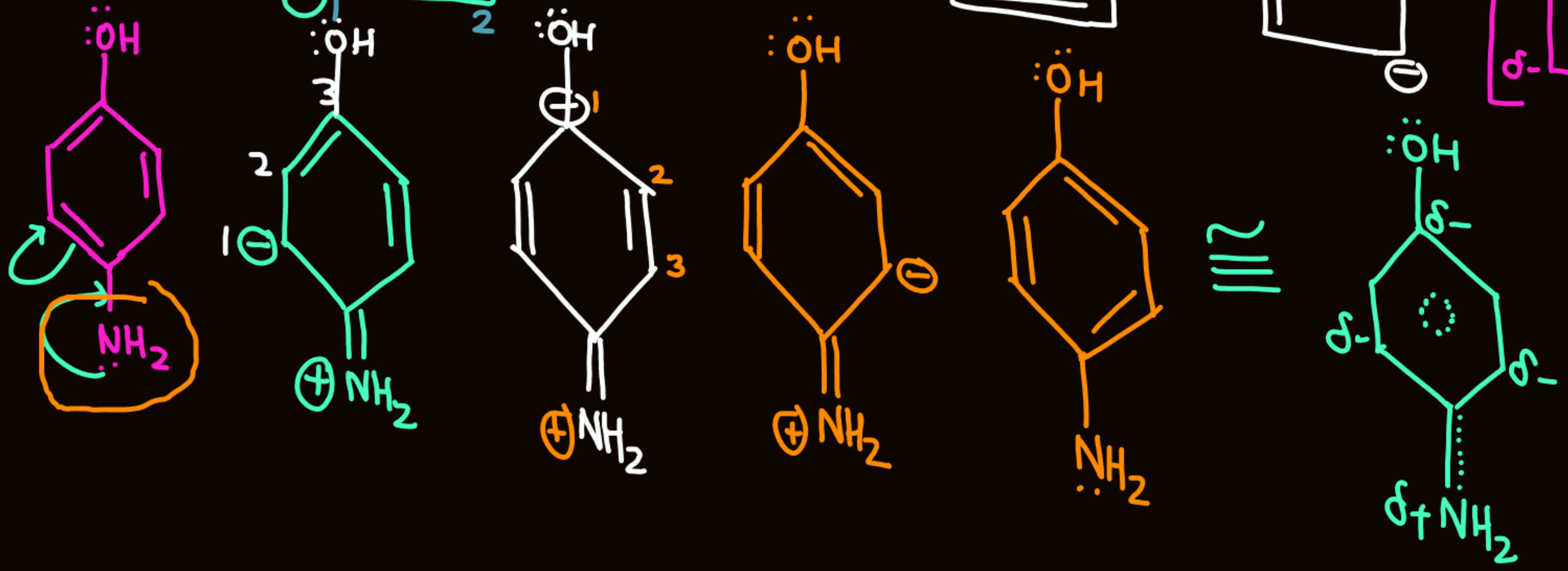
Q5
5RS



Q6



Q7



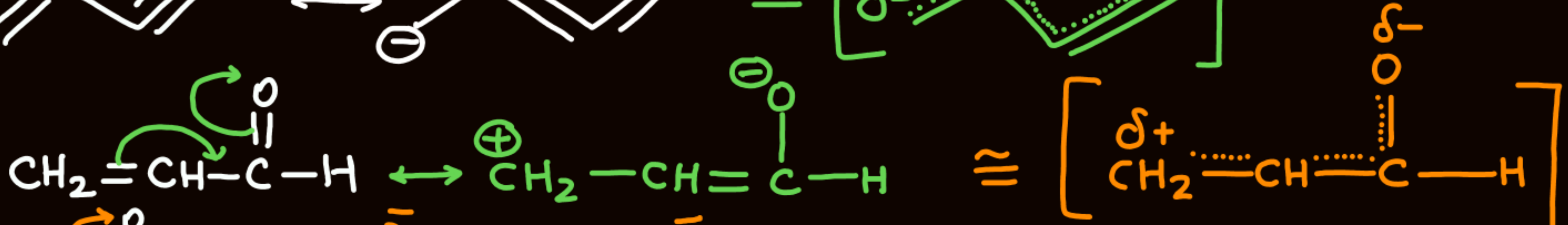
2RS
Q8



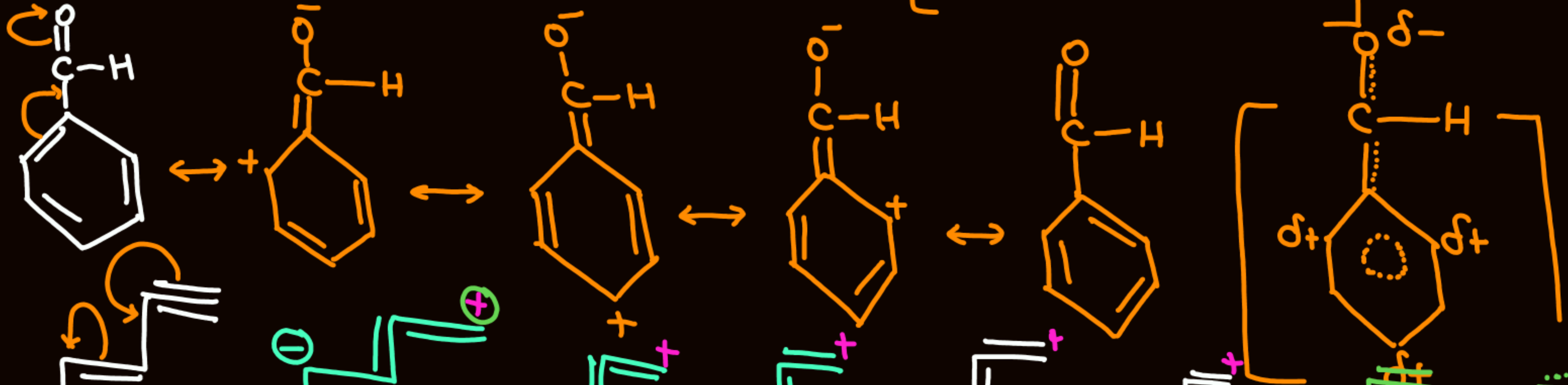
2RS
Q9



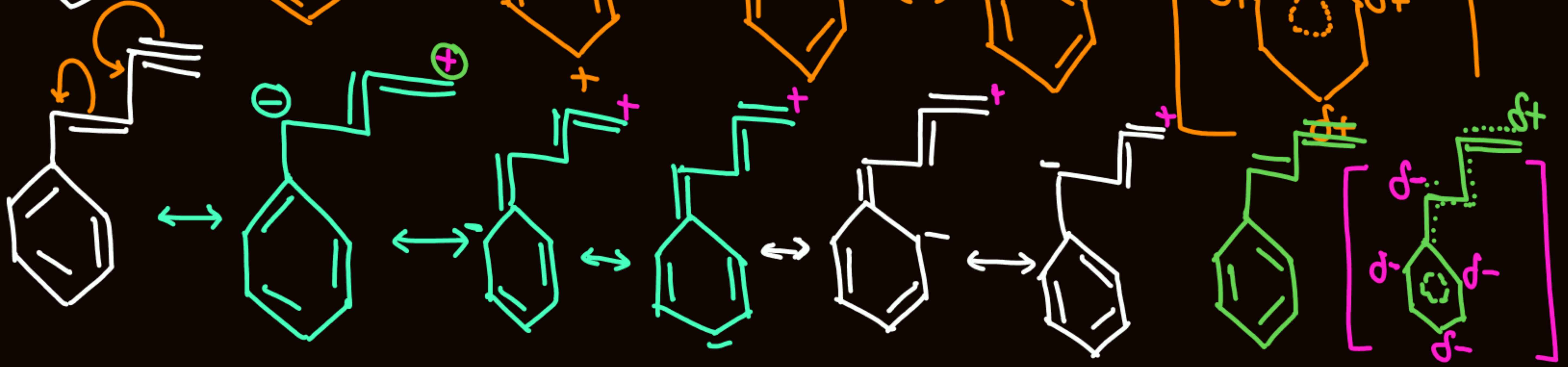
2RS
Q10



Q11
5RS



Q12
7RS



Q13

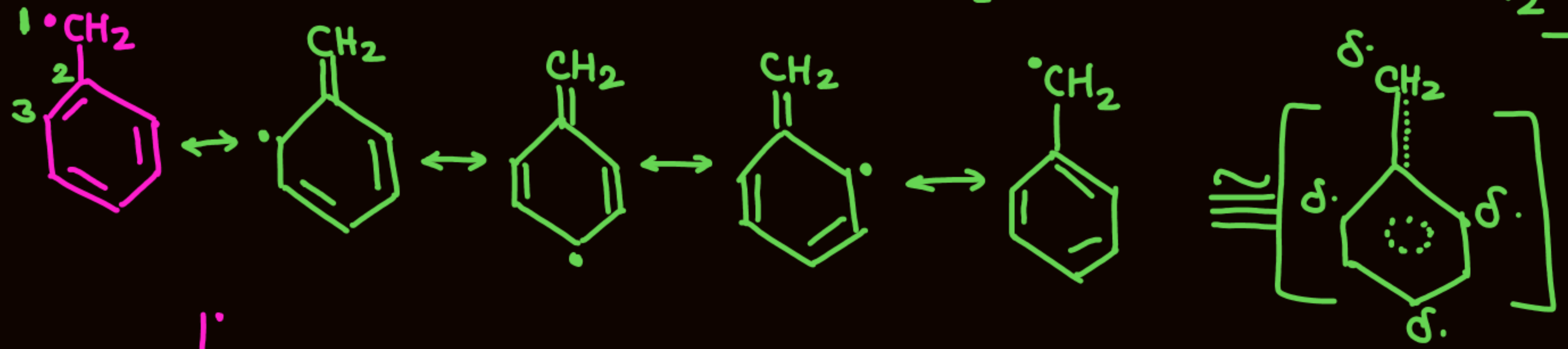
$$\underset{3}{CH_2}=\underset{2}{CH}-\underset{1}{\dot{C}H_2} \longleftrightarrow \dot{C}H_2-CH=CH_2 \cong \left[\overset{\delta\cdot}{C}H_2 \overset{\cdots}{—} CH \overset{\cdots}{—} \overset{\delta\cdot}{C}H_2\right]$$

Q14

$$CH_2=CH-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{\dot{C}H_2} \longleftrightarrow \underset{3}{CH_2}=\underset{2}{CH}-\underset{1}{\dot{C}H}-CH=CH_2 \longleftrightarrow \dot{C}H_2-CH=CH-CH=CH_2$$

$$\left[\overset{\delta\cdot}{C}H_2 \overset{\cdots}{—} CH \overset{\cdots}{—} \overset{\delta\cdot}{C}H \overset{\cdots}{—} CH \overset{\cdots}{—} \overset{\delta\cdot}{C}H_2\right]$$

Q15



Q16

HW



7RS

$p\pi-p\pi$ Resonance / $p\pi-d\pi$ Reso

→ one atom should be donor.
Other atom " " acceptor.

$\overset{+}{C}H_2-\ddot{\underset{..}{O}}H \longleftrightarrow CH_2=\overset{+}{\underset{..}{O}}H$ $p\pi-p\pi$

$\overset{+}{C}H_2-\ddot{N}H_2 \longleftrightarrow CH_2=\overset{+}{N}H_2$ $p\pi-p\pi$

$\overset{+}{C}H_2-\ddot{\underset{..}{F}}: \longleftrightarrow$ No Reso

→ Highest electronegative
→ can not donate lp.

$\overset{+}{C}H_2-\ddot{\underset{..}{Cl}}: \longrightarrow CH_2=\overset{+}{\underset{..}{Cl}}:$ $p\pi-p\pi$ Reso (Cl donates lp 3p orbital)

$\overset{+}{C}H_2-\ddot{\underset{..}{S}}H \longleftrightarrow CH_2=\overset{+}{\underset{..}{S}}H$ $p\pi-p\pi$ Reso

$\overset{+}{C}H_2-\ddot{P}H_2 \longleftrightarrow CH_2=\overset{+}{P}H_2$ $p\pi-p\pi$ Reso

$\bar{C}H_2 - \ddot{O}H \rightarrow$ X

$\bar{C}H_2 - \ddot{N}H_2 \rightarrow$ X

$\bar{C}H_2 - \ddot{F}: \rightarrow$ X

$\bar{C}H_2 - \ddot{Cl}: \rightarrow CH_2 = \overline{Cl}$

$\rightarrow$ Cl → Vacant d orbital accepts lp of C → $p\pi - d\pi$ Reso

$\bar{C}H_2 - \ddot{S}H \rightarrow CH_2 = \overline{S}H$

$\rightarrow p\pi - d\pi$

$\bar{C}H_2 - \ddot{P}H_2 \rightarrow CH_2 = \overline{P}H_2$

$\rightarrow p\pi - d\pi$

NOTE → Due to Resonance, Single bond becomes Strong (Single bond ⟶ partial double bond)

Double bond becomes Weak (Double bond → partial double bond)

NOTE → Due to Resonance, Single bond (Bond length ↓) (Single bond ⟶ partial double bond)

Double bond (Bond length ↑) (Double bond → partial double bond)

Bond Strength: Triple bond > partial triple bond > Double bond > partial double bond > Single bond

Bond Length: Triple bond < partial triple bond < Double bond < partial double bond < Single bond

$$\text{Bond Strength} \propto \frac{1}{\text{Bond length}}$$

Stability of Resonating str

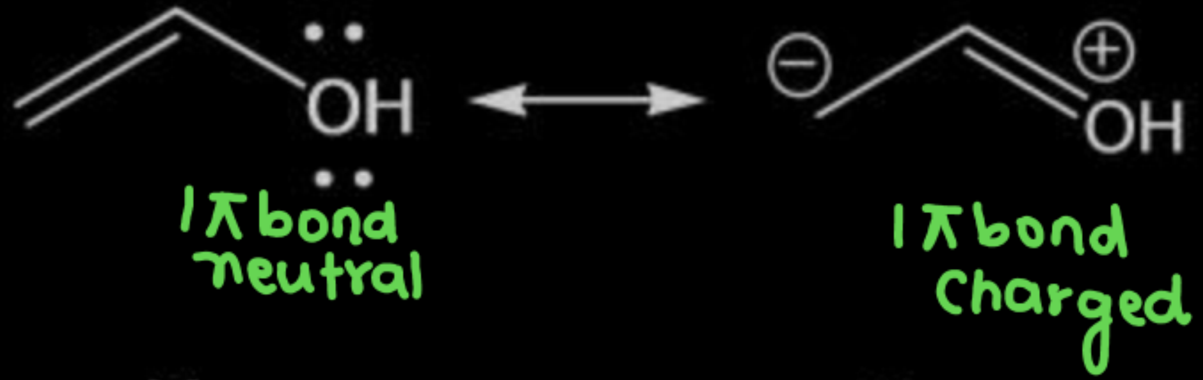
1. Resonating str having more pi bond is more stable.
2. Neutral Resonating str is more stable than charged.
3. Resonating str having octet complete of all atom is more stable.
4. Negative charge on more EN is more Stable; +ve Charge on less EN is more stable.
5. opposite charges when near to eachother is more stable & Same charge when away from eachother is more stable.
6. Stability ∝ number of Benzenoid Ring
7. If conjugation is Same then Linear Conjugation is more stable than cross Conjugation.
8. If conjugation is Same then aromatic is more Stable than normal Comp.

Q. Which is more stable among them:

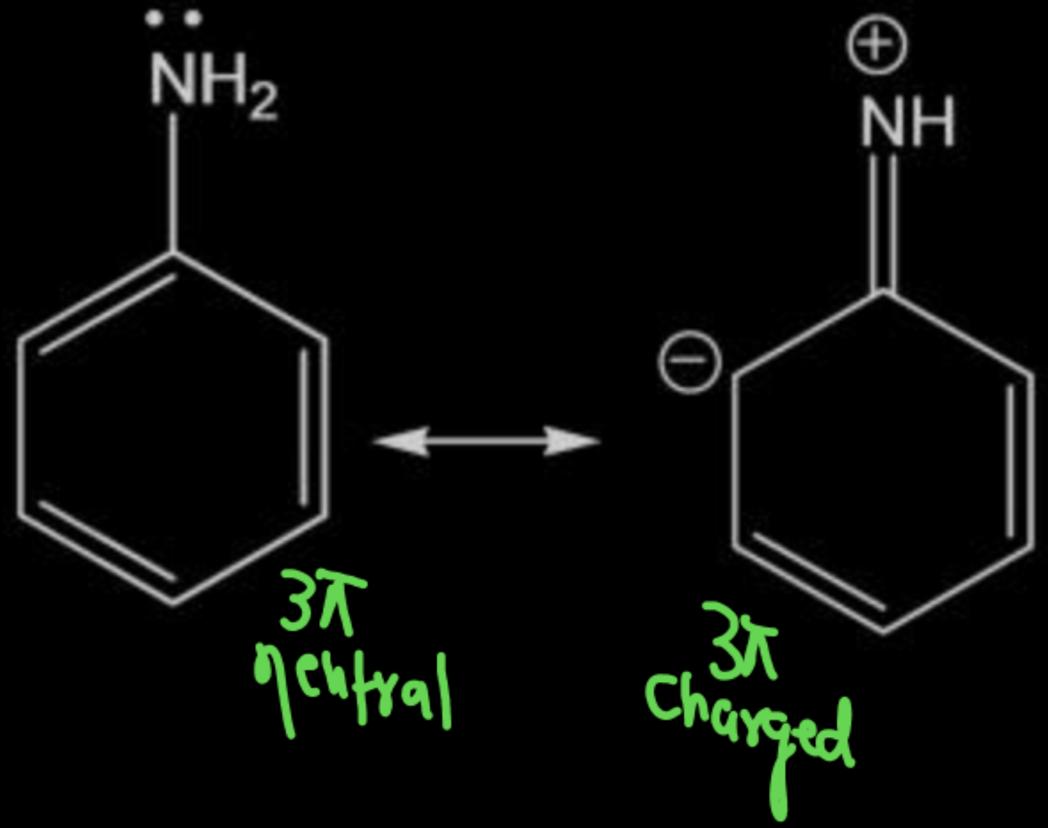
(1) $CH_2{=}CH{-}CH{=}O \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH{-}O^{\ominus}$

2π bond   1 bond

1 > 2

(2) 

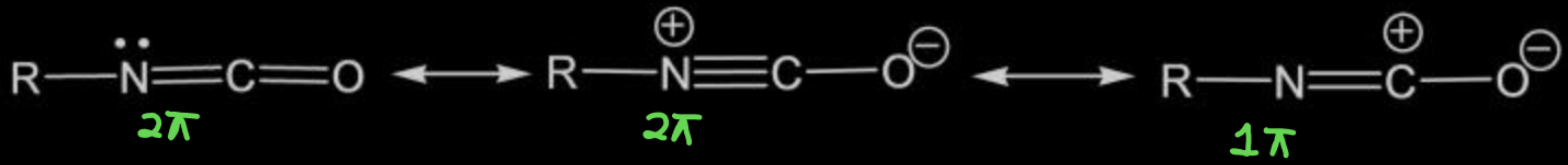
1 > 2

(3) 

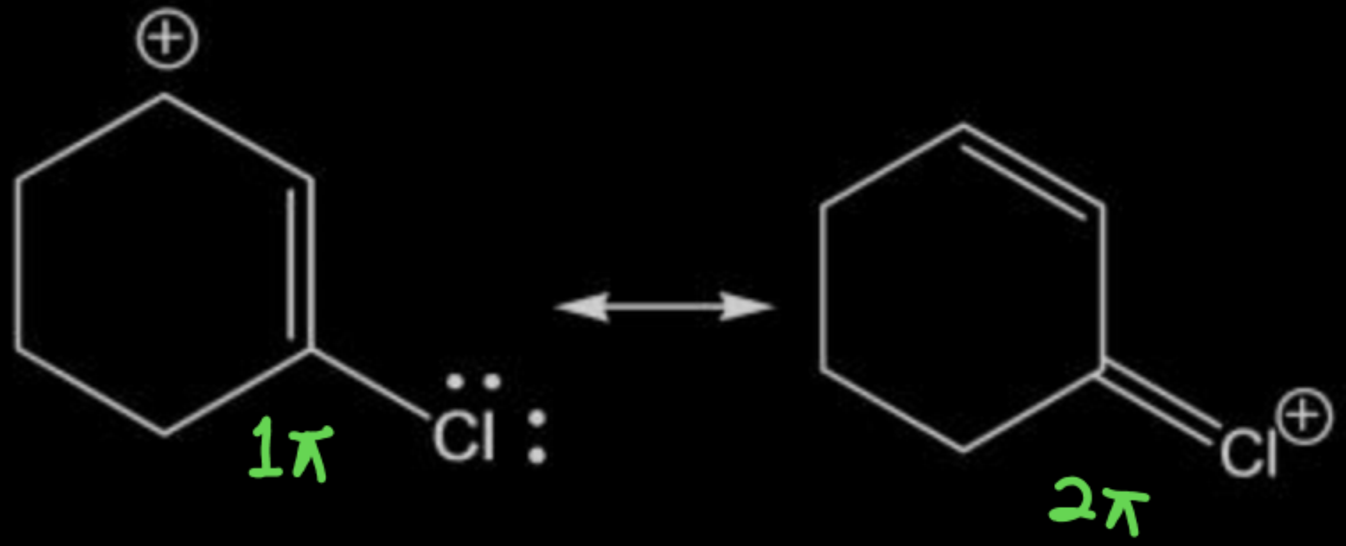
1>2

1>2>3

(4)

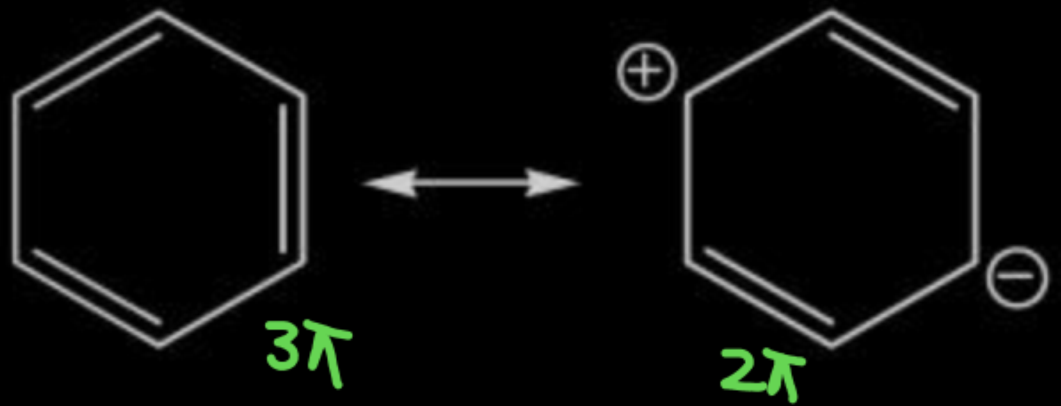


(5)



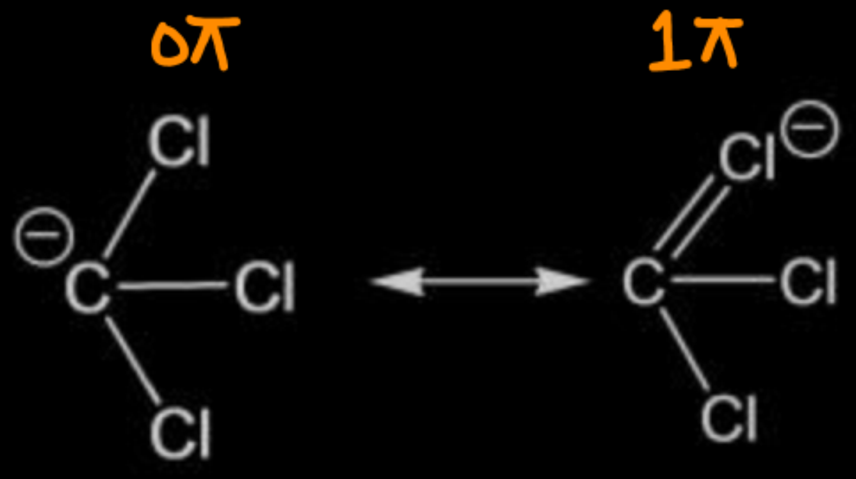
2>1

(6)



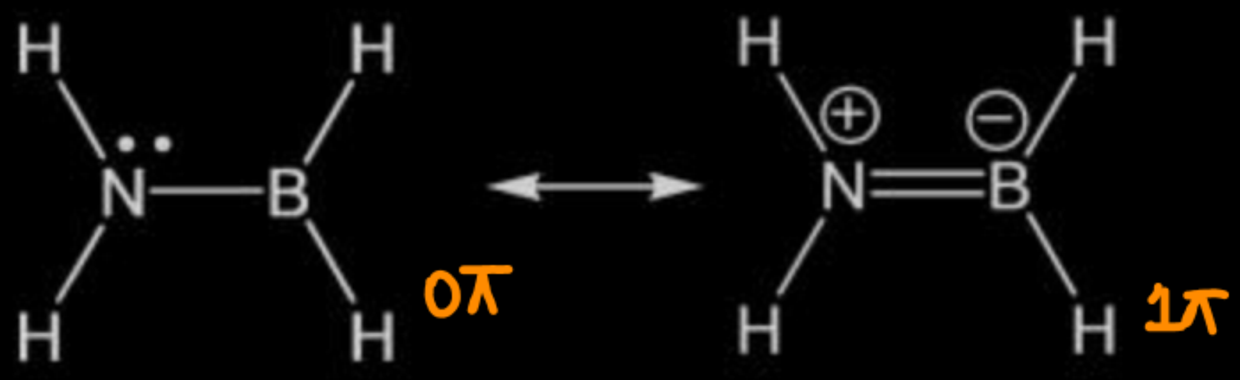
1>2

(7)



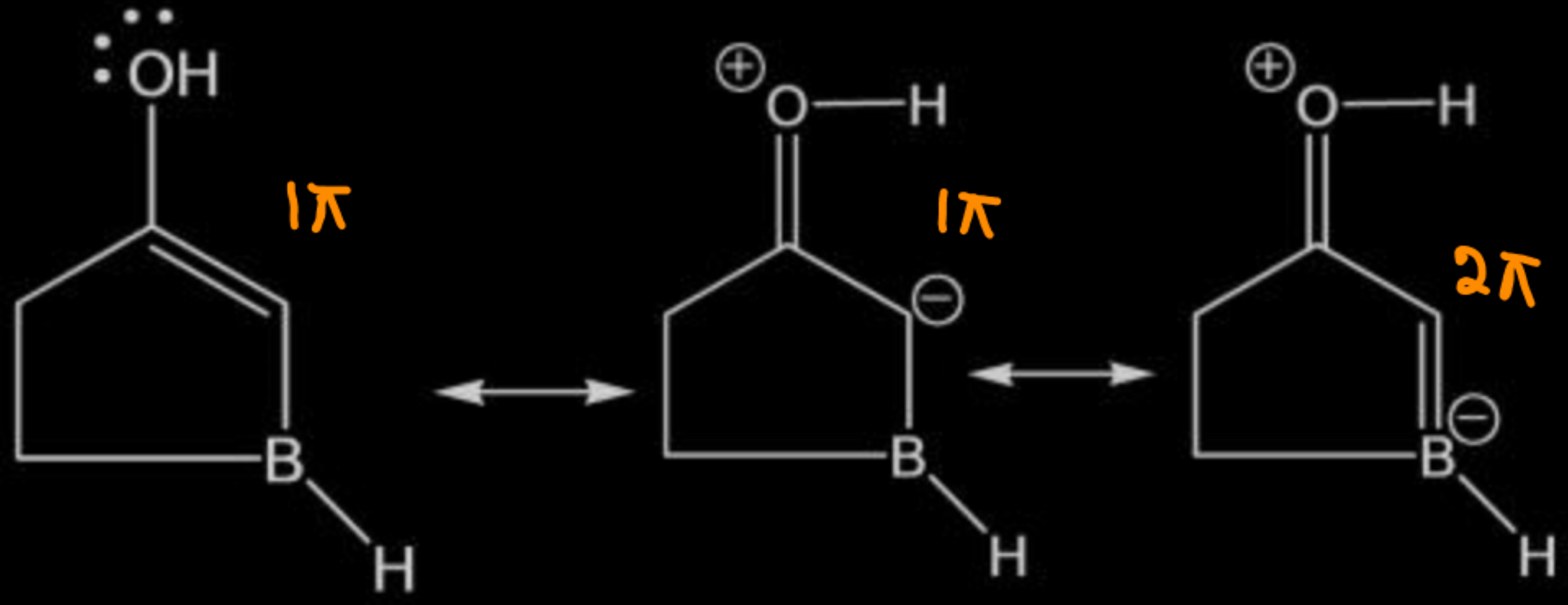
2>1

(8)



2>1

(9)



3>1>2

$I \approx S \approx C$ En Same

(10) $CH_3-\overset{\oplus}{C}=\ddot{\underset{\cdot\cdot}{O}}$ ⟷ $CH_3-C\equiv O^{\oplus}$

1π 2π

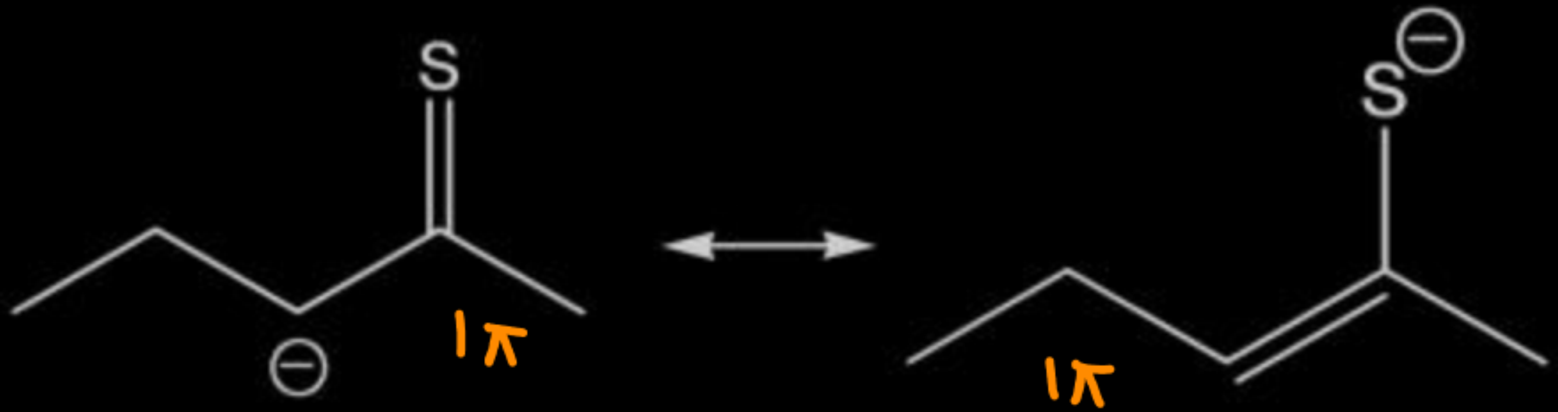
2 > 1

(11) $CH_2=CH-O^{\ominus}$ ⟷ $\overset{\ominus}{C}H_2-CH=O$

1π 1π

1 > 2

(12)

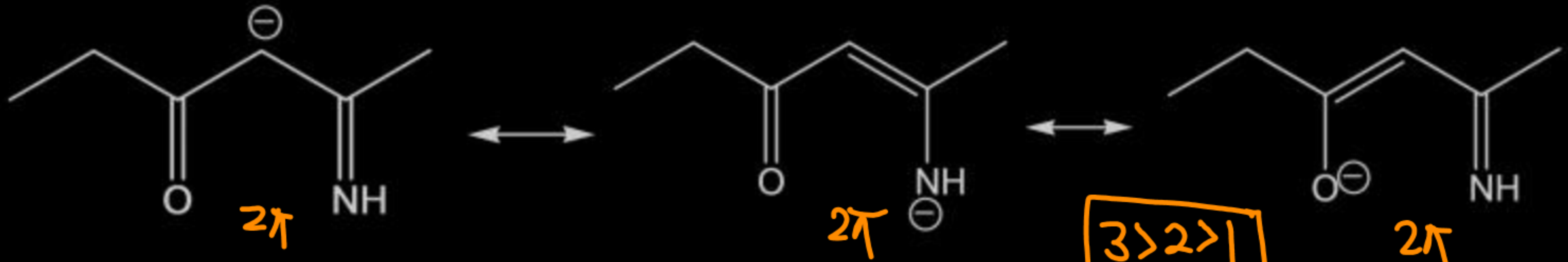


2 > 1

-ve Charge → Small Size → Repulsion

-ve charge → Big Size → less Repulsion

(13)



3 > 2 > 1

(14) $CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH_3$

(π σ π) ... (π σ π σ π)

2>1 (more Reso → more stab)

(15)



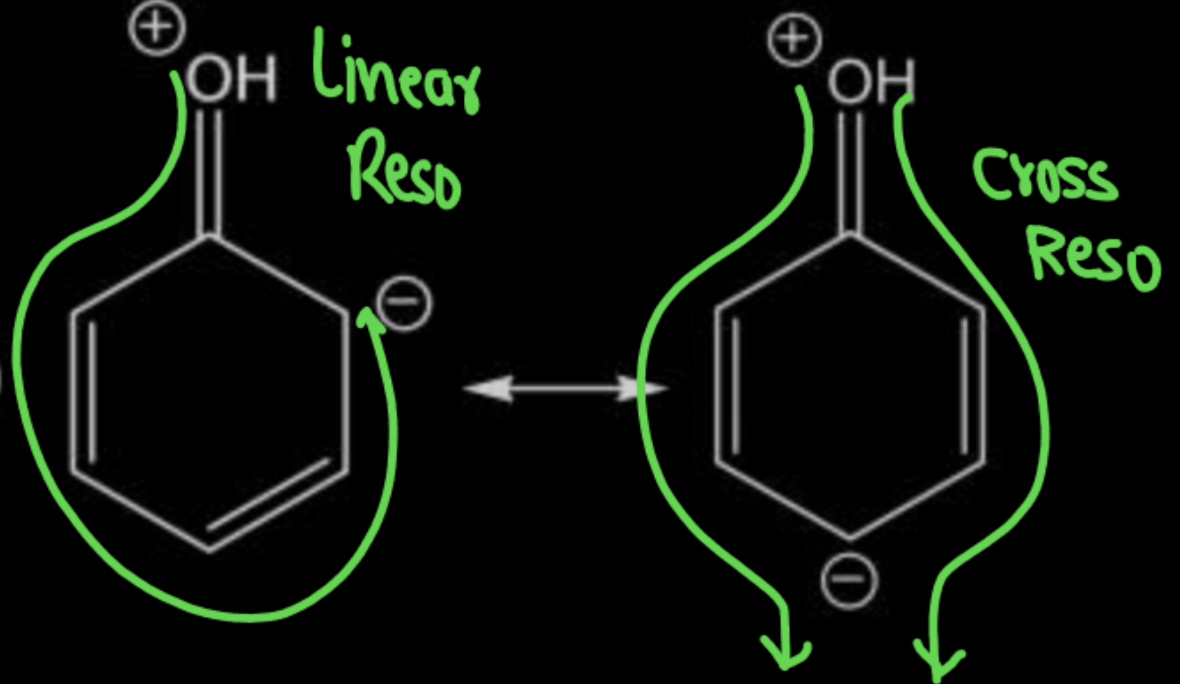
(I) (II)

(if amt of Reso → same)
(Aromatic > normal str)
2 > 1

(16) $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}C({=}CH_2){-}CH{=}CH_2$

Linear Resonance 1>2 Cross Resonance

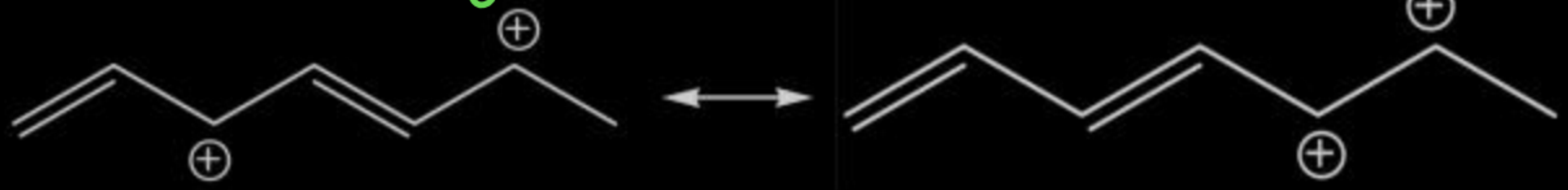
(17)



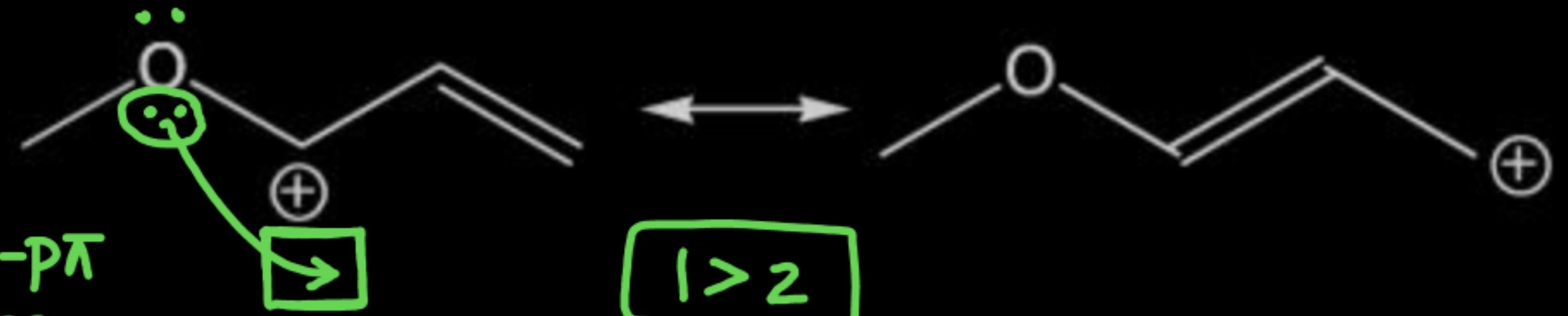
1>2

if amount of Resonance ↓ Linear Reso > Cross Reso

Same charge → Faraway | Same charge → near

(18) 

1>2

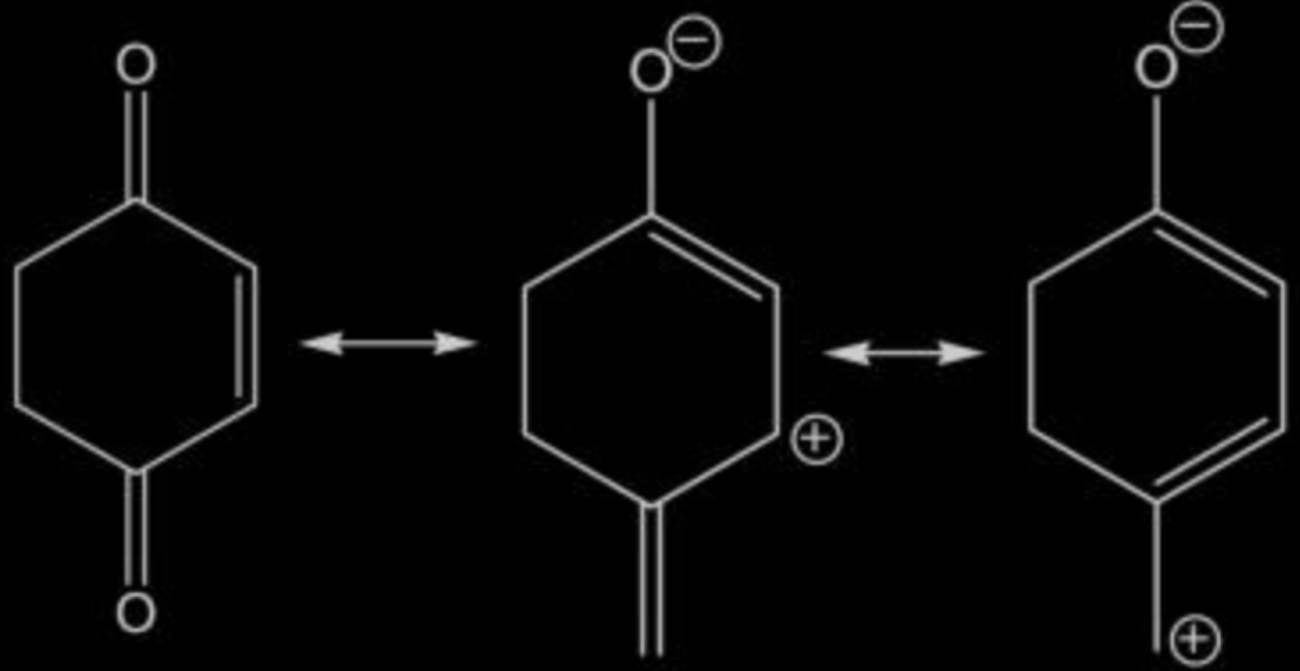
(19) 

Pπ-Pπ Reso

1>2

(20) $CH_3-\overset{\oplus}{C}H-CH=CH-O^{\ominus} \longleftrightarrow CH_3-CH=\overset{\oplus}{C}H-CH-O^{\ominus}$

1>2

(21) 

1>2>3

Mesomeric Effect

THANK YOU

All the Best!!

GOC

↓

Aromaticity

Mesomeric

Aroma = Smell/ Flavour

Aromaticity

Aromatic Compound

- Cyclic
- Resonance in complete cycle
- planar (sp/sp^2 atom)
- Huckel's Rule

Follows $(4n+2)\pi e^-$

n=0	$2\pi e^-$	1 pair πe^-
n=1	$6\pi e^-$	3 pair πe^-
n=2	$10\pi e^-$	5 pair πe^-
n=3	$14\pi e^-$	7 pair πe^-
⋮	⋮	

CROP → odd Pair πe^-

- Diamagnetic

Antiaromatic Compound

- Cyclic
- Resonance in Complete cycle
- planar (sp/sp^2 atom)

Huckel's Rule → $(4n\pi e^-)$

n=1	$4\pi e^-$	2 pair πe^-
n=2	$8\pi e^-$	4 pair πe^-
n=3	$12\pi e^-$	6 pair πe^-
n=4	$16\pi e^-$	8 pair πe^-
⋮	⋮	

CREP → Even pair of pi electron.

- Paramagnetic

Nonaromatic Compound

- cyclic/acyclic
- Complete Resonance not present.

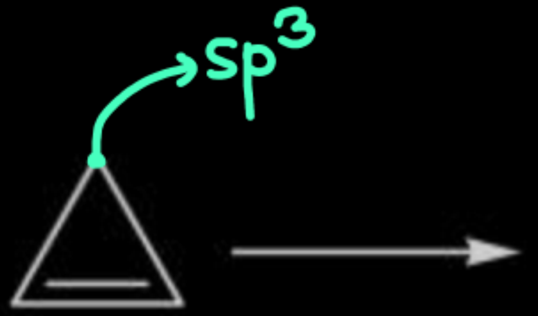
or (sp^3 atom → nonaromatic)

Stability → Aromatic > Non Aromatic > Anti Aromatic

(A) > (NA) > (AA)

A > NA > AA

Ques. Classify the following compounds as Aromatic, Anti-aromatic, Non-aromatic.

(1) 

Cyclopropene

C
R ✗

(NA)

(2) 

Cyclopropenyl cation

C
R
1 pair

crop (A)

(3) 

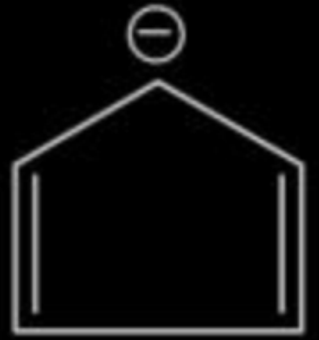
Cyclopropenyl anion

C
R
2 pair

crep (AA)

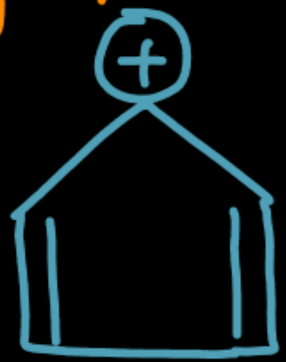
note → when lp / -ve charge is in Resonance then lp's -ve charge is treated as 1 extra pair of πe^-

(8) Cyclopentadienyl cation

(4) 

→ C R 3pair crop (A)

Cyclopentadienyl anion



C R ep → (AA)

2pair

Only 1 lp → Reso

(5) 

→ (2pair) C R ep (AA)

1 lp → Resonance ✓ → delocalised lp

1 lp → Resonance ✗ → localised lp

(6) 

→ 3pair C R op (A)

(7) 

→ 3pair C R op (A)

Pyridine

pyridine → lp donot participate in Resonance.

→ lp → localised.

(8) 

pyrole

→ 3pair
C
R
OP
(A)

lp → delocalised

3pair



C
R
OP
(A)

Furan

3Pair

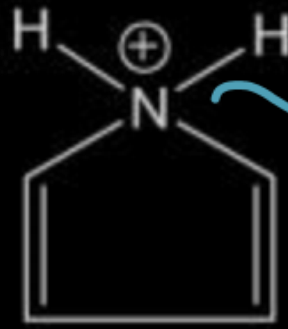


C
R
OP
(A)

Thiophene

(9) 

→ 2pair
C
R
ep
(AA)

(10) 

→ sp^3

(NA)

(11) 

Tropolium cation

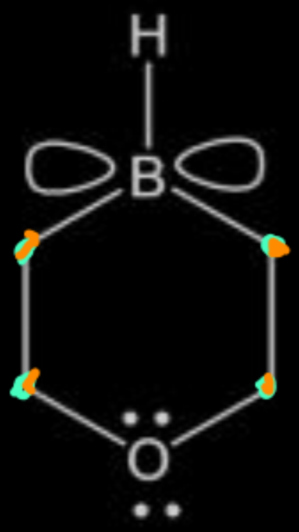
→ 3pair
C
R
op
(A)

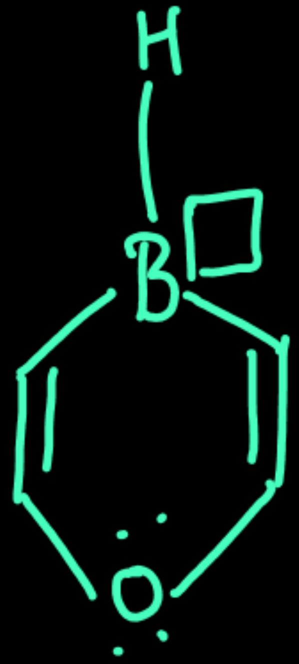
(12)  → 4pair C R ep → (AA)

(13)  → (NA)

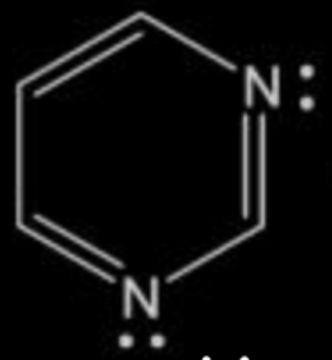
→ All Free Radicals are non Aromatic.

(14)  → 1pair C R op (A)

(15)  → sp^3 atom → (NA)

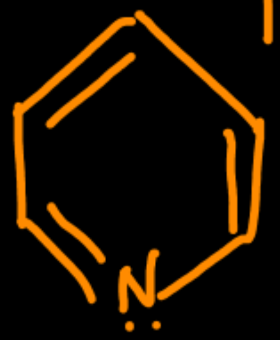
(16) 

~~3pair~~
C
R
op
(A)

(16) 

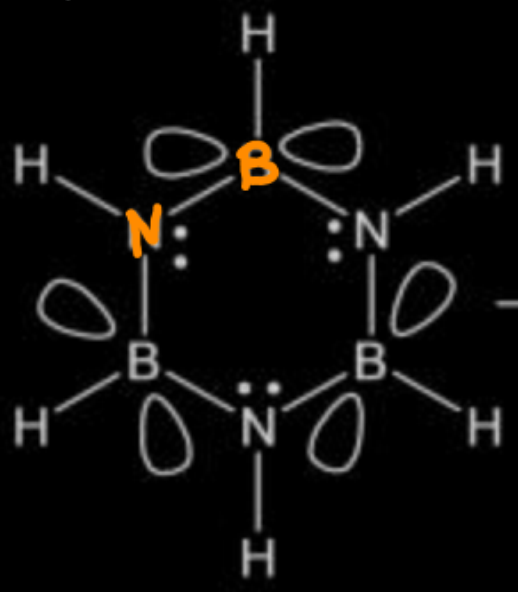
Pyrimidine

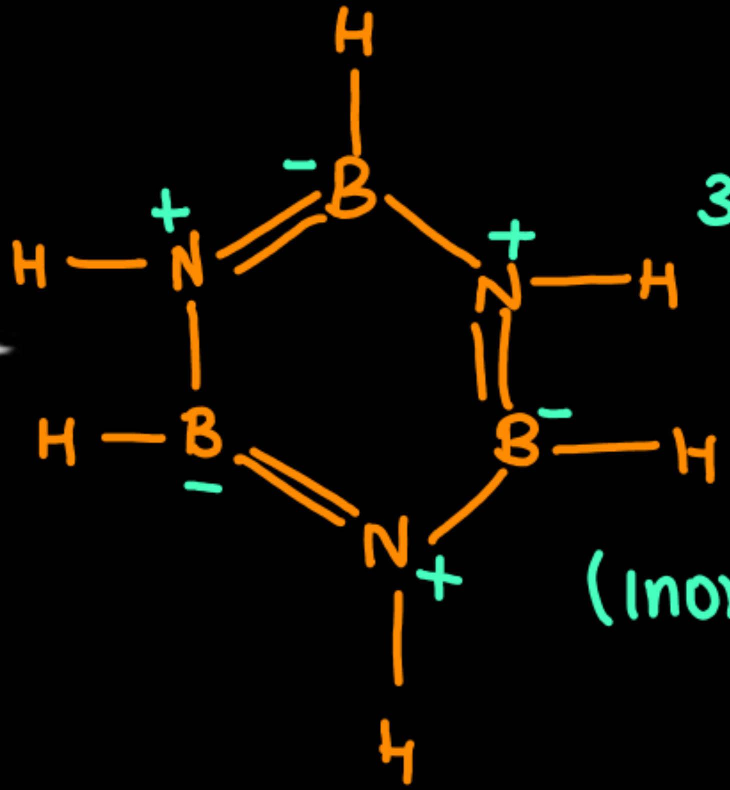
→ 3pair C R Op → (A)



Pyridine

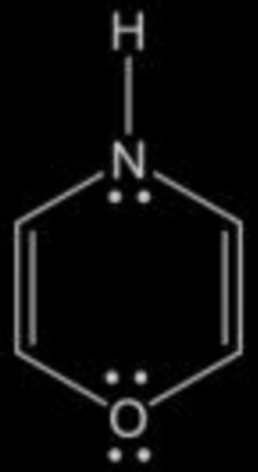
3pair C R Op → (A)

(17) 

→ 

3pair C R Op → A

(Inorganic Benzene) ($B_3N_3H_6$)

(18) 

→ 4pair C R ep (AA)

(20)  → 3 pair, odd pair; C, R, op → A

Tropolium

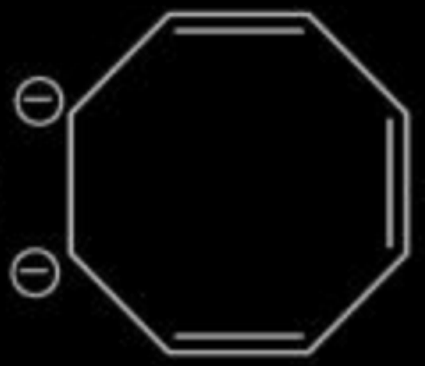
NOTE → 8 member or bigger Ring if it is Anti Aromatic then comp changes to non Aromatic.

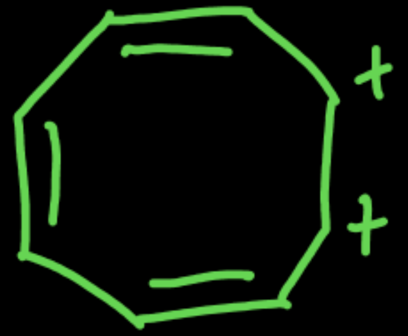
(21)  →  (out of plane) → NA

Cyclooctatetraene (COT)

AA → NA Final Ans

TUB Shape str

(22)  → C, R, 5 pair op → A

23  C, R, 3 pair op → A

24  sp3 → NA

Annulene

Annulene[8],[10][12] → plane change
↳ NA

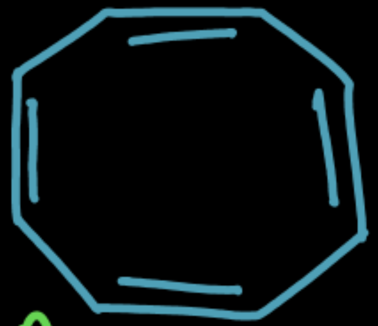
Monocyclic Ring with alternate pi bond is k/a annulene (name → Annulene[x])
↳ No of Carbon in Ring


Annulene[4]

C
R — AA
ep


Annulene[6]

C
R — A
op


Annulene[8]

C
R — AA → (NA) Tubshape
ep



Annulene[10]

H-H Repulsion → Plane changes → (NA)



Annulene[12]
H-H Repulsion
↓
Plane change
↓
(NA)



Annulene[14]
C
R
7pair OP → (A)
(no Repulsion)
(Big Ring)

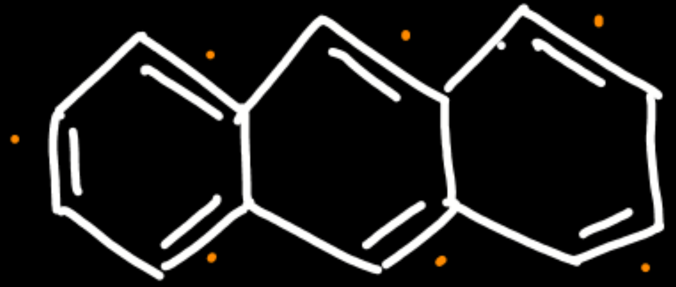
Polycyclic Ring

In case of more than one Ring → only boundary πe^- are counted for Huckel's Rule.



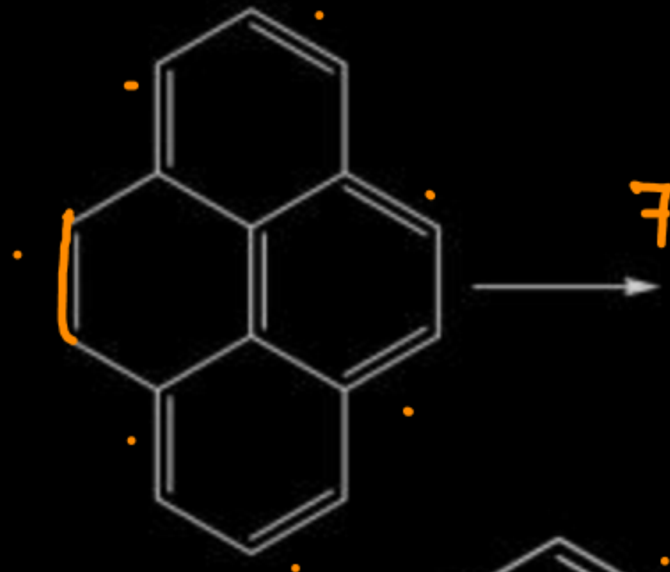
nepthalene

5pair C R Op (A)

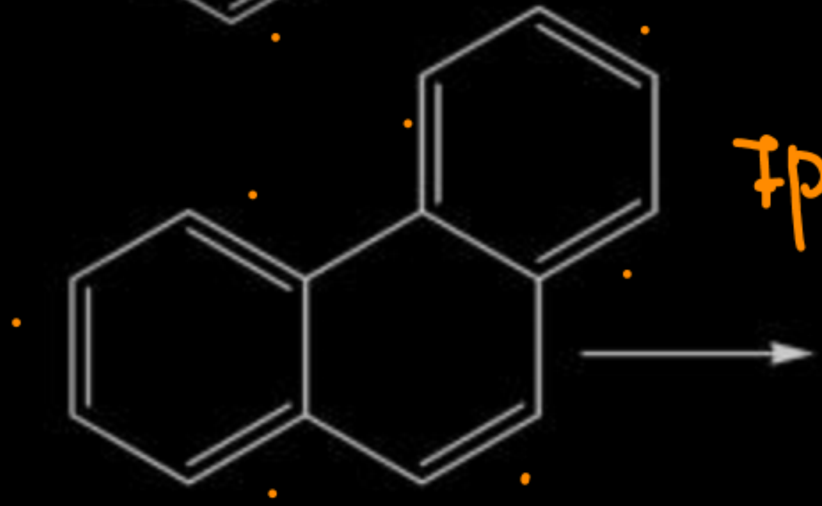


Athracene

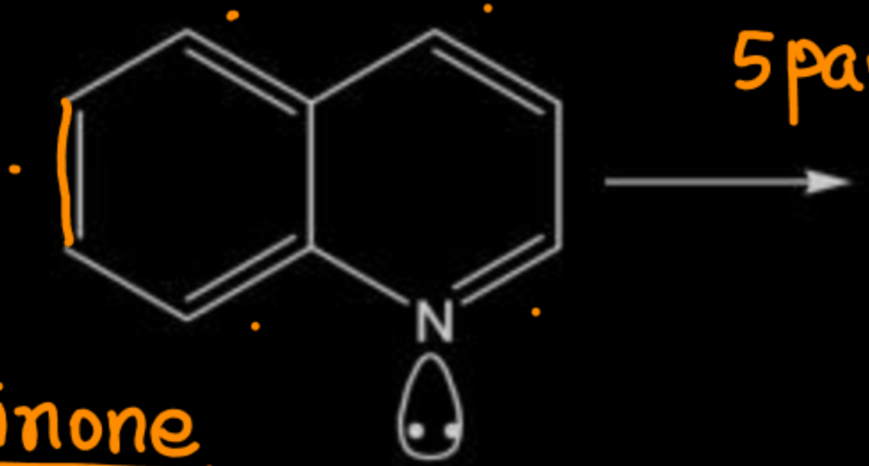
7pair C R Op (A)

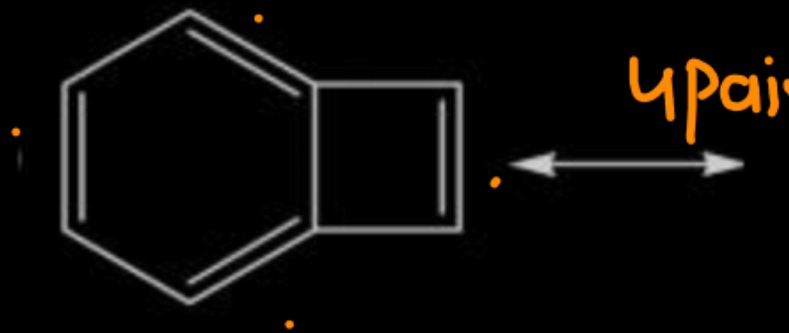


7pair C R Op (A)



7pair C R Op (A)

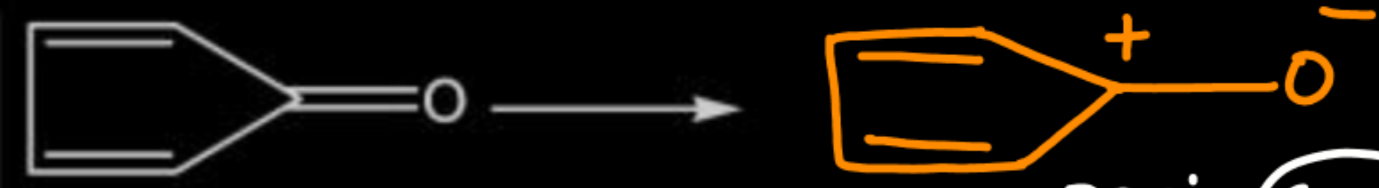

Quinone
N
5pair
C
R
OP
A


4pair
C
R
ep
AA

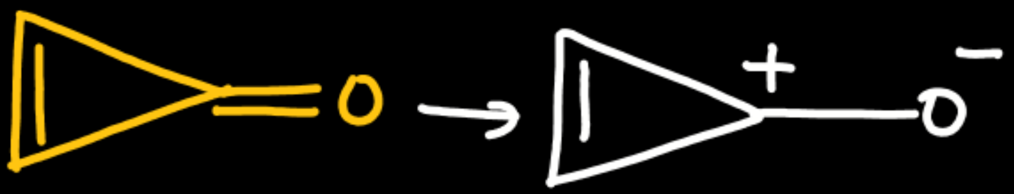

azulene
5pair
C
r
op
A

Quasi-Aromatic

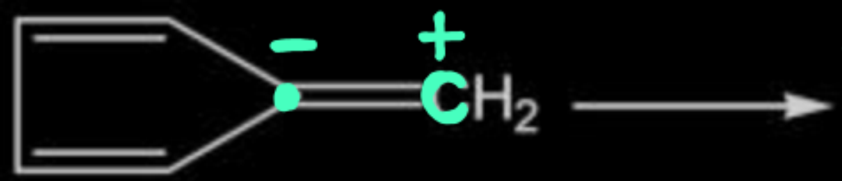
Aromaticity is present with involvement of charge → Quasi Aromatic



Q2

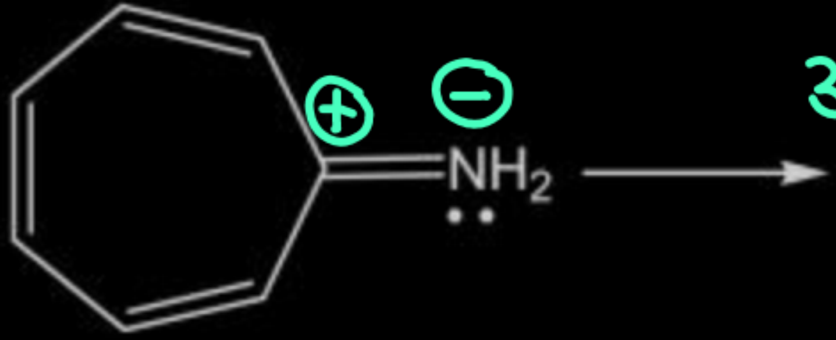


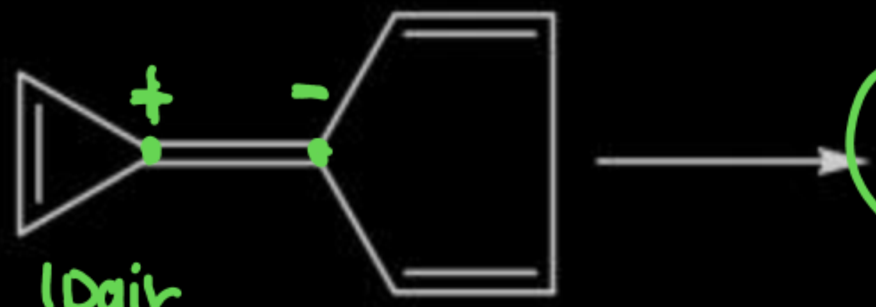
*



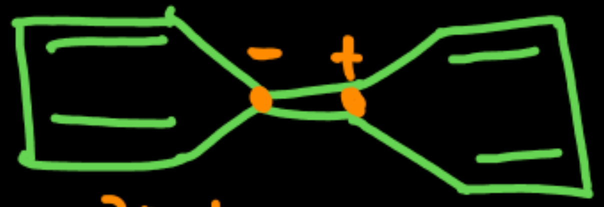
Q3

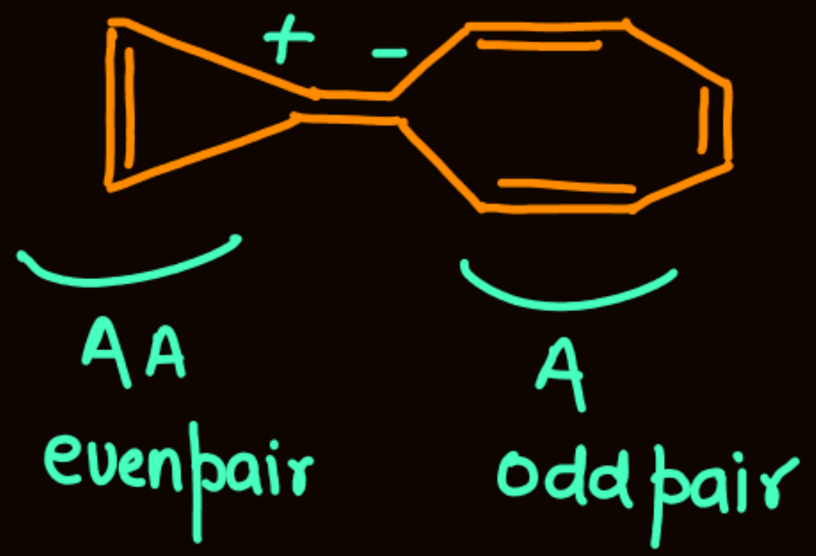




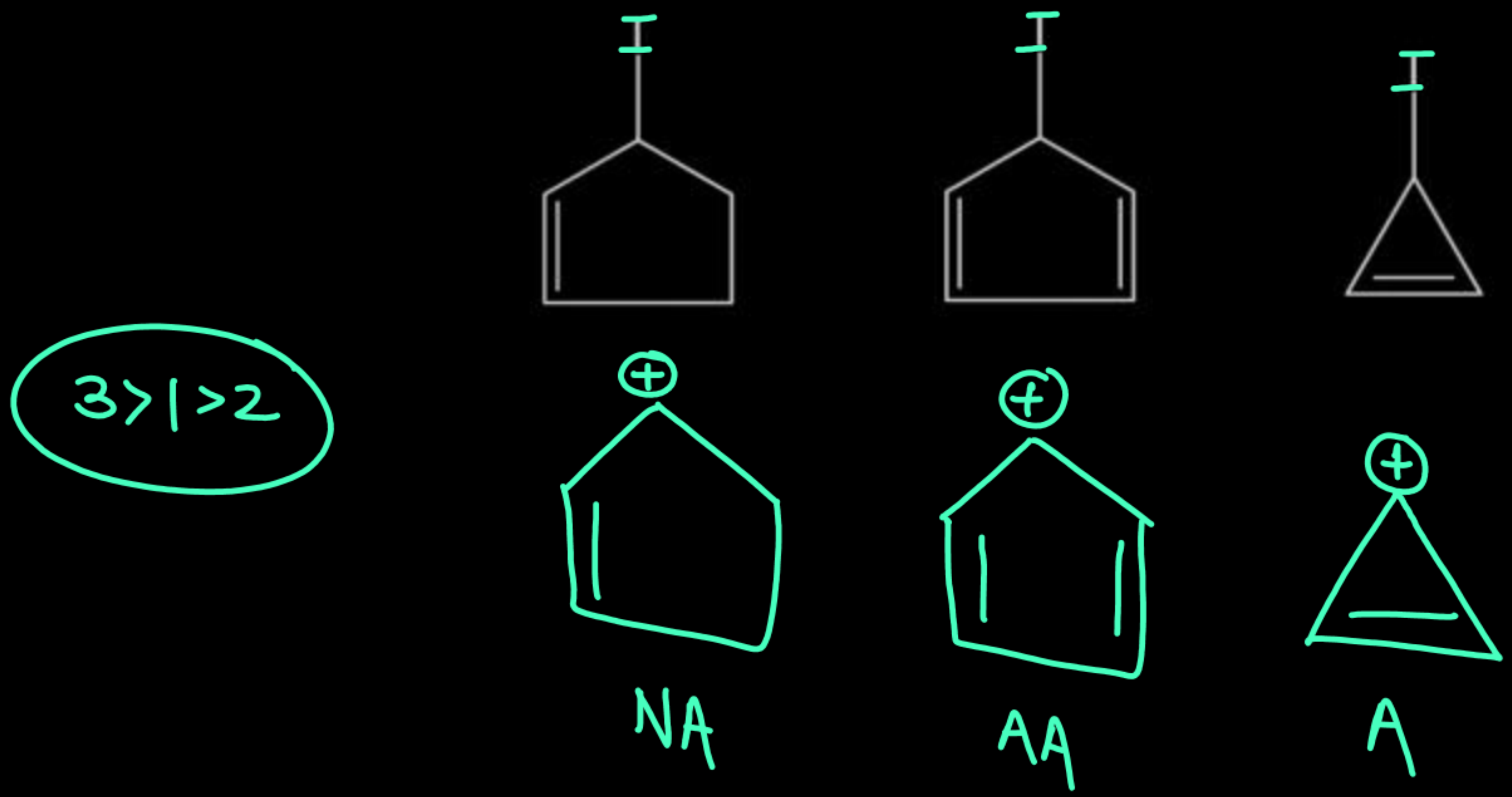


Que

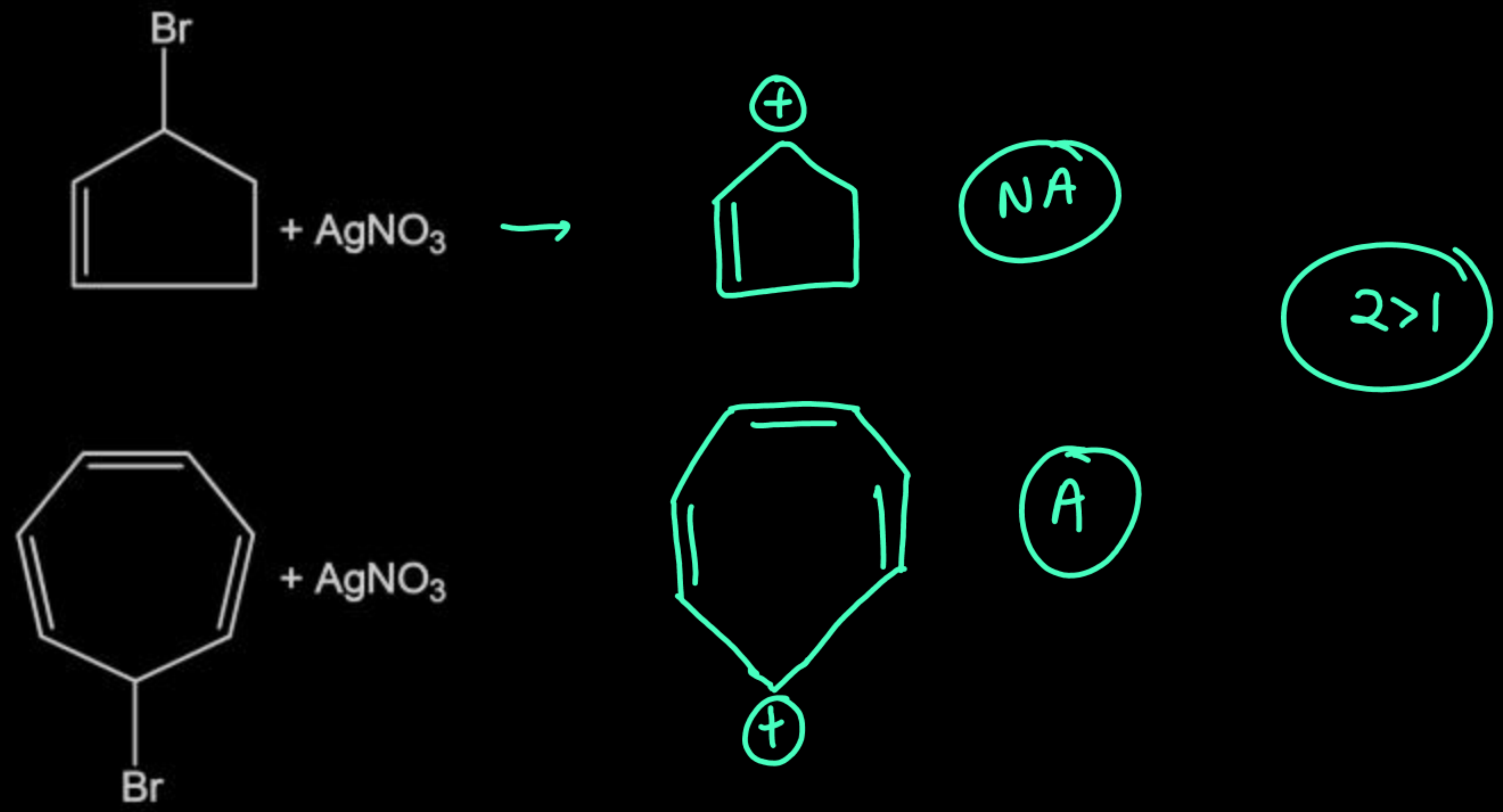



+
−
AA
even pair
A
odd pair

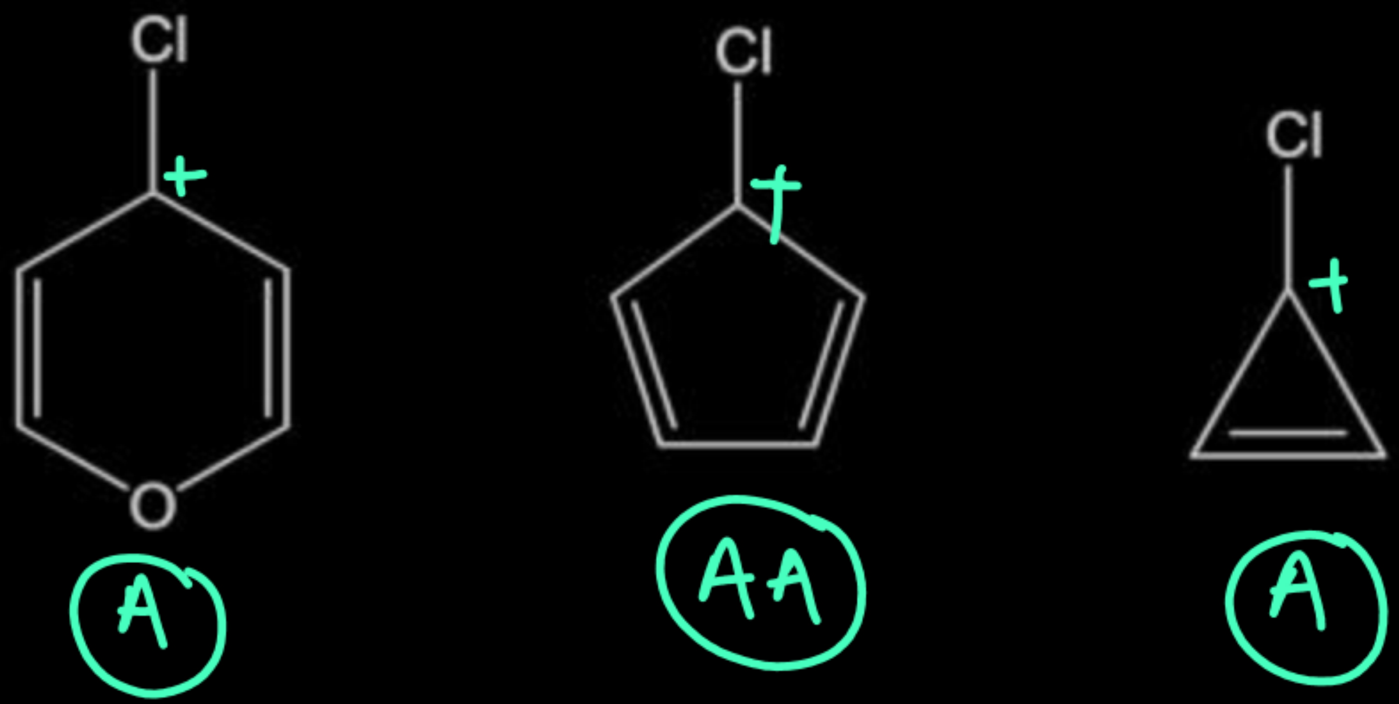
(Q) Compare rate of abstraction of $I^{\ominus}$



(Q) Compare the rate of ppt. formation



(Q) Compare rate of reaction with $AgNO_3$ ($Ag^+ Cl^-$)



$1 > 3 > 2$

1hr {

6hr

6·30 – 7·30 (1Hour)

8 — 2

3·30 – 5·30 (2Hour) — 30min notes Revise
— 1·30hr Que prac → 40Que

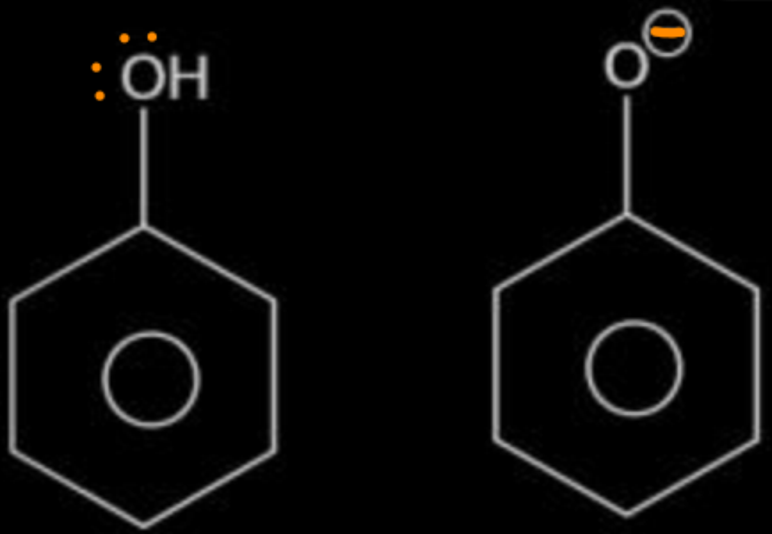
6·30 – 8·30 (2hour) — 30min
— 1·30hr → 55-60Que

10·00 – 12·00 (2hour) → 75-80 Que

THANK YOU
All the Best!!

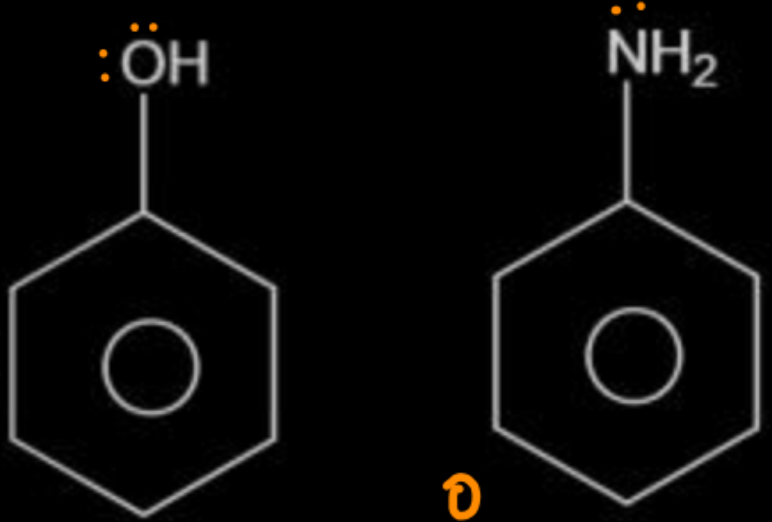
Compare +M/−M Effect

(1)



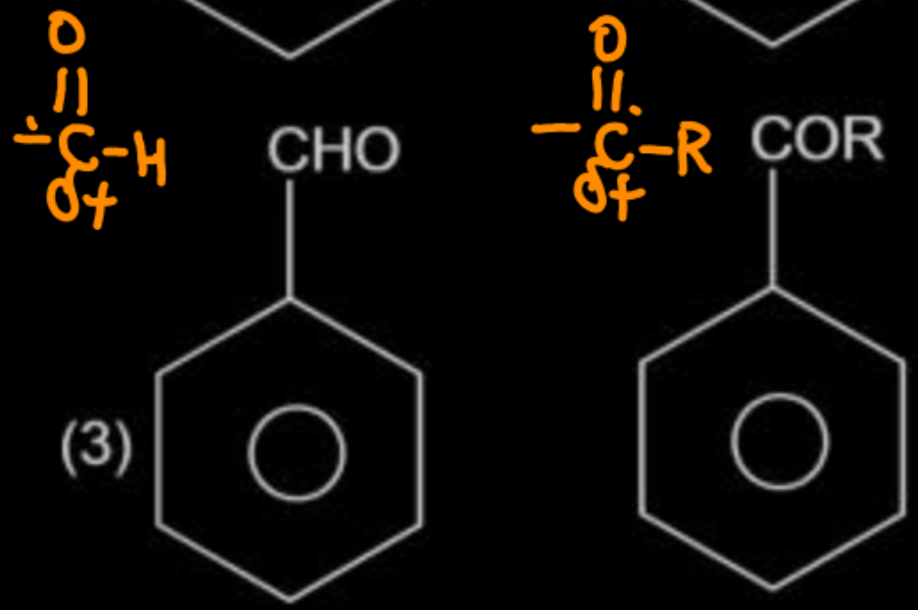
b>a

(2)



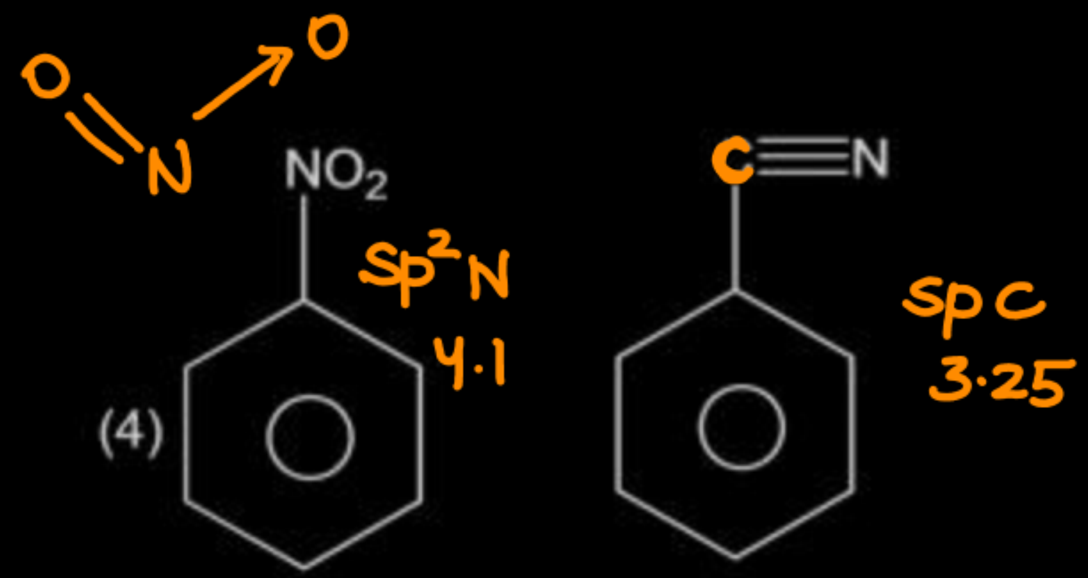
b>a

(3)



1>2

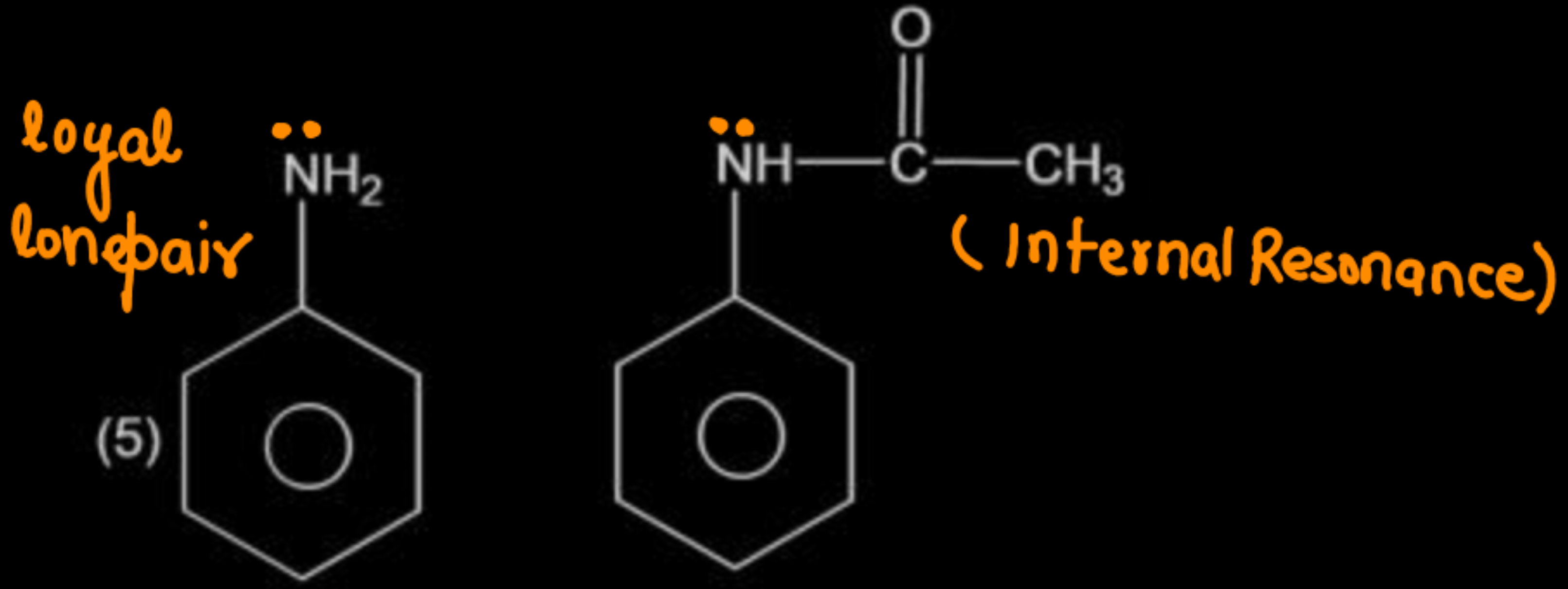
(4)



O
N
O
NO2
sp2 N
4.1
C≡N
sp C
3.25

a > b

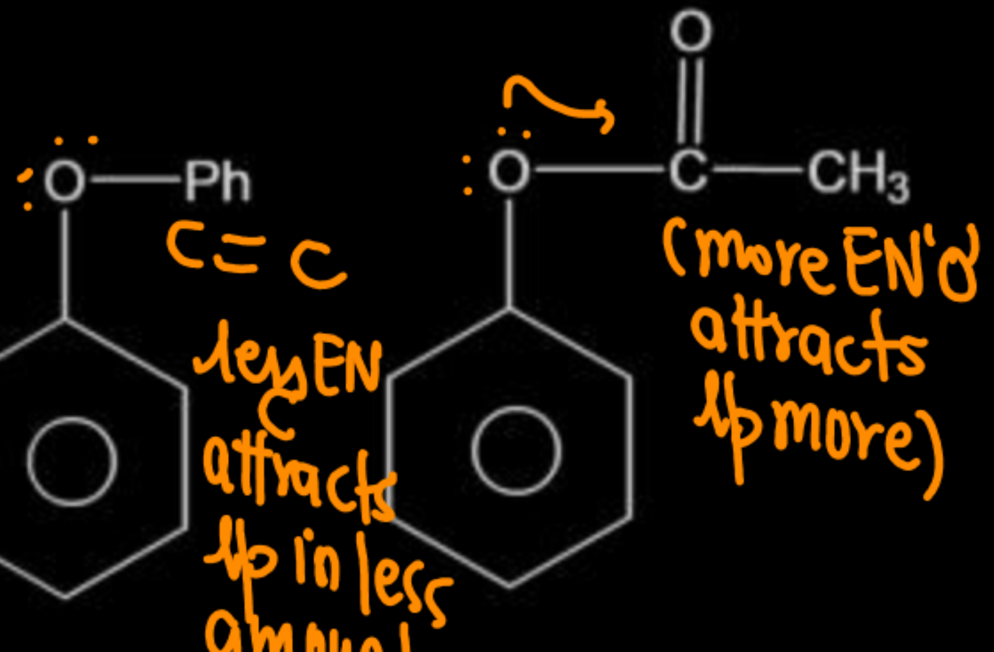
(5)



loyal lonepair
NH2
NH—C—CH3
O
(Internal Resonance)

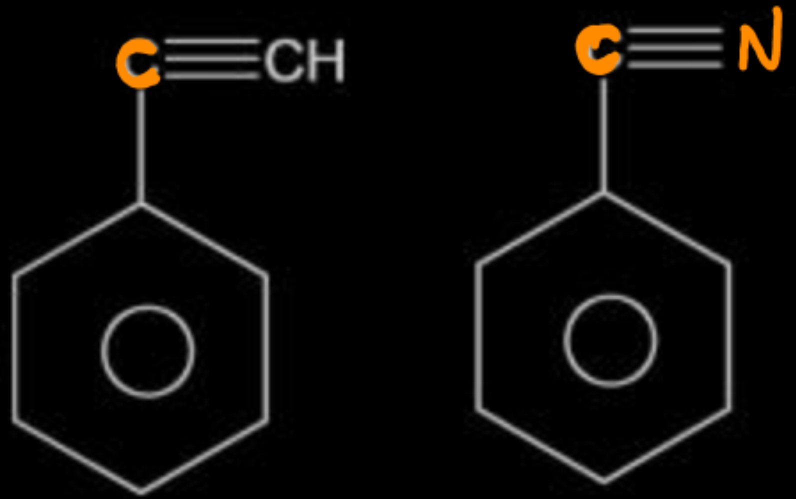
a > b

(6)



O—Ph
C=C
less EN C attracts lp in less amount
O—C—CH3
O
(more EN'O' attracts lp more)

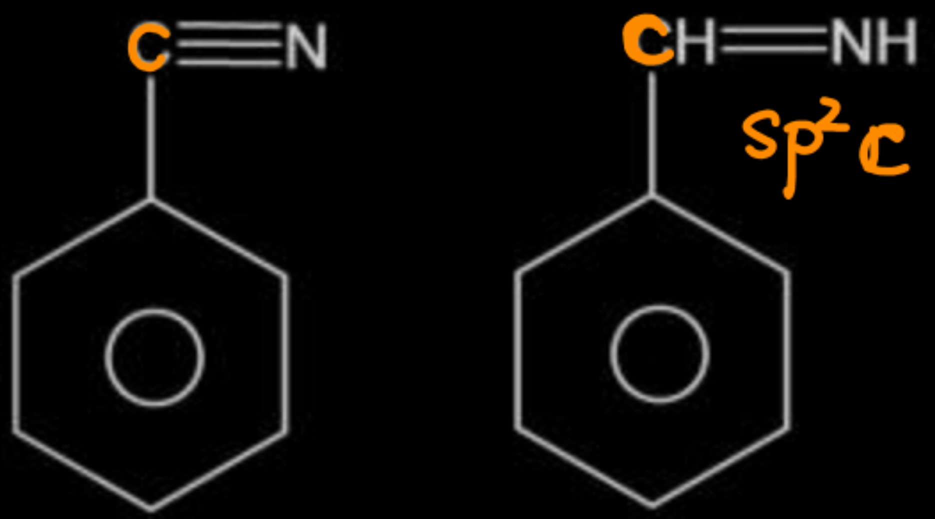
a > b

(7)


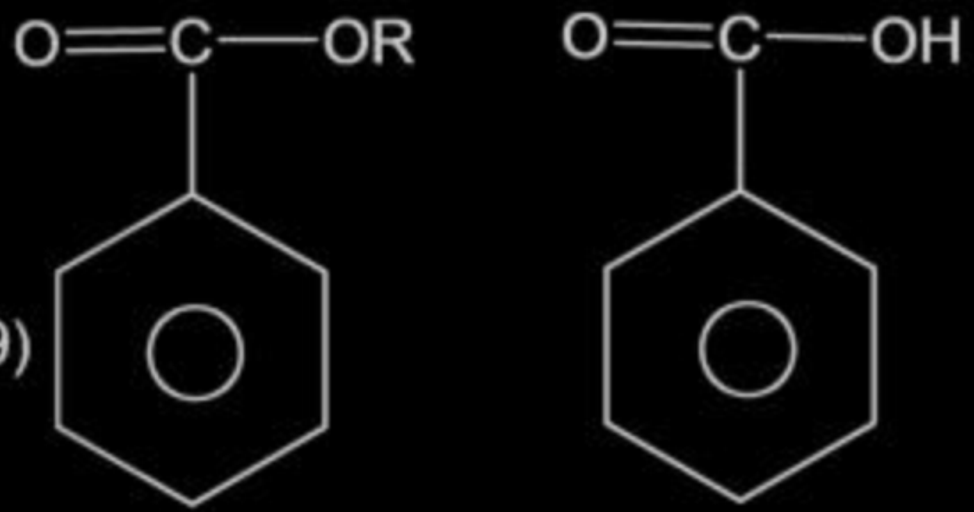
(more EN
more -M)

b>a

spc

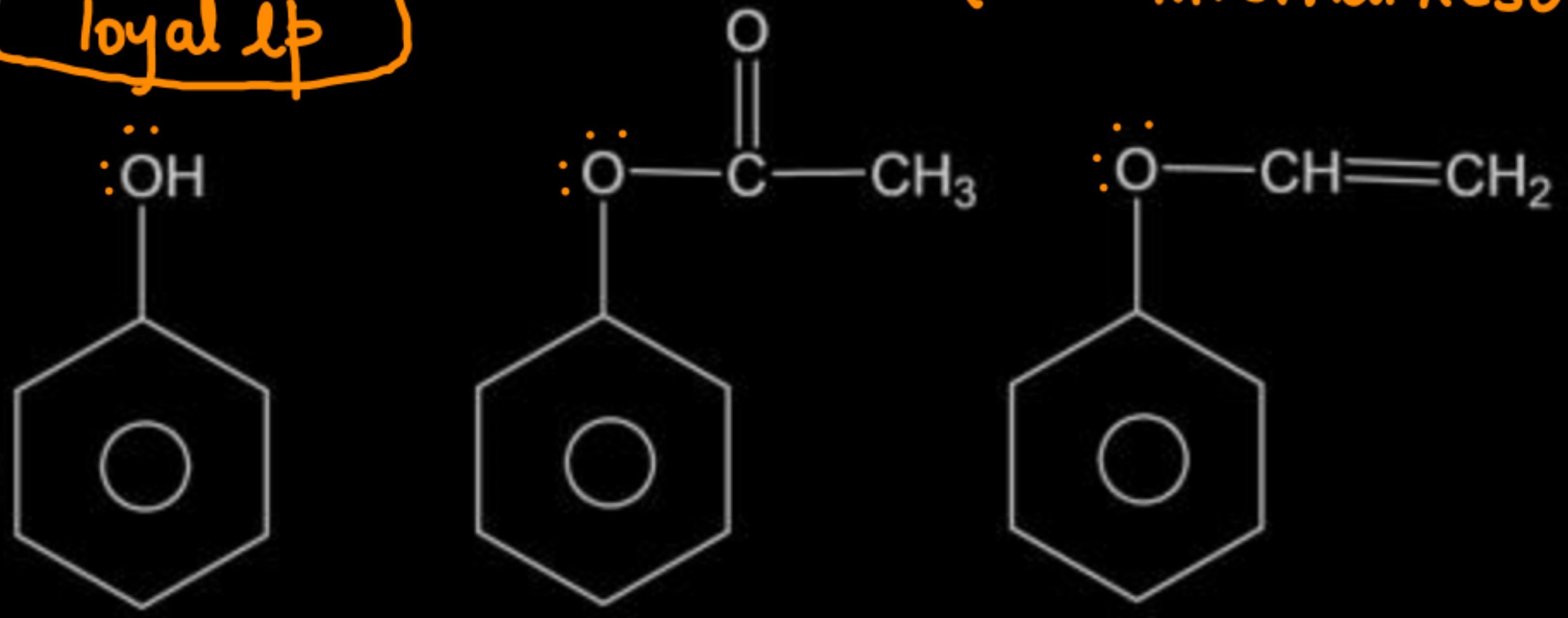
(8)


a>b

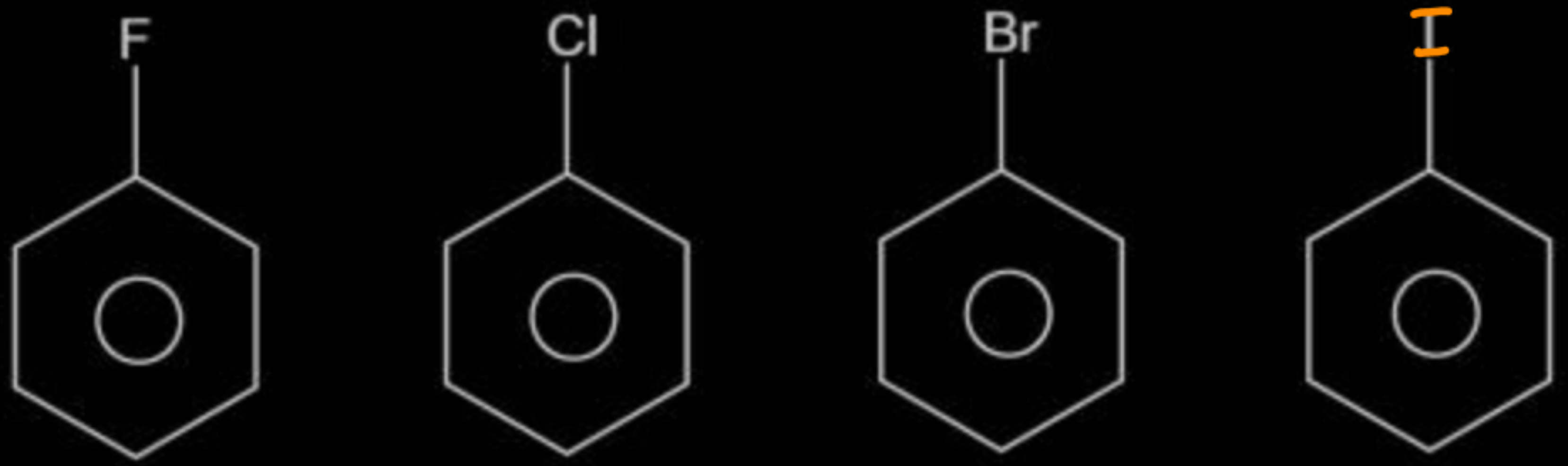
(9)


b>a

loyal lp — Internal Reso(more) — Internal Reso(less)

(10) 

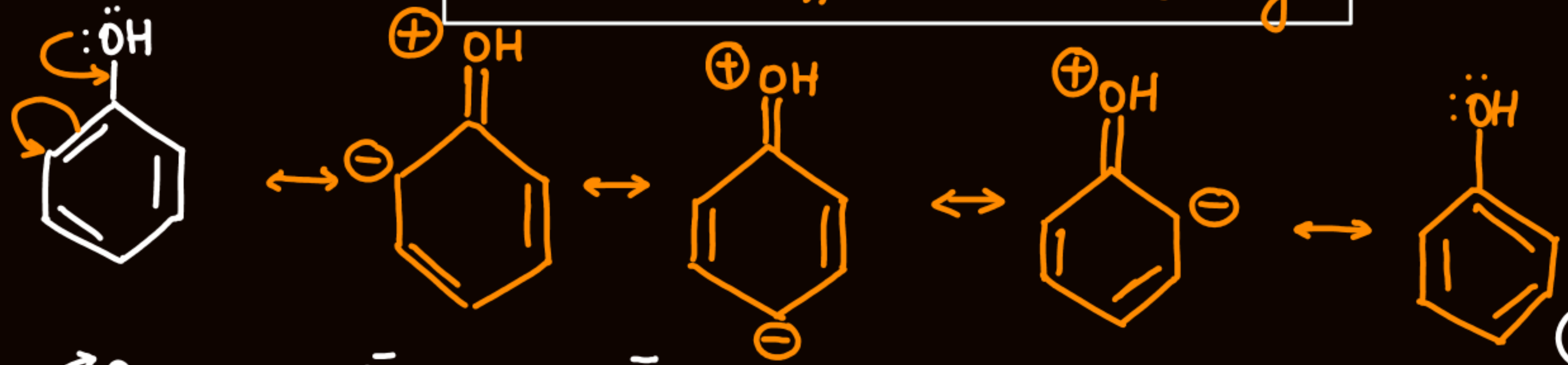
1 > 3 > 2

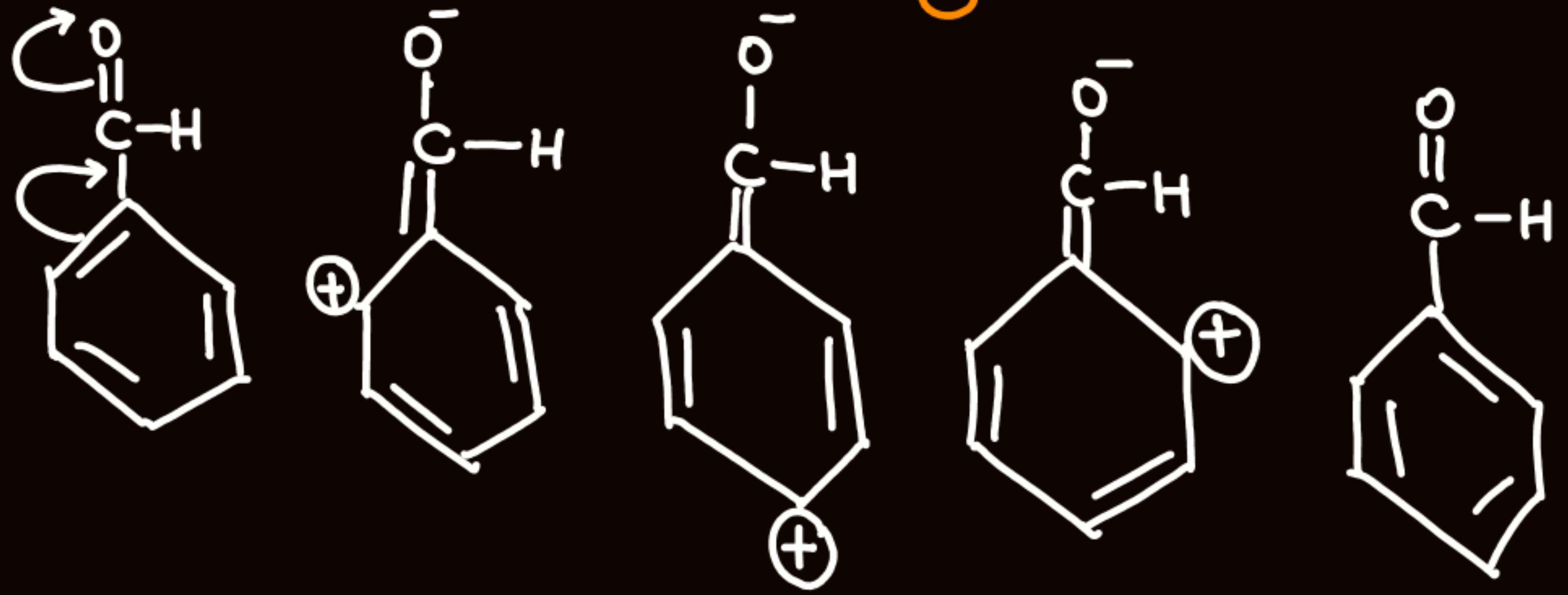
(11) 

<u>note</u> In case of Halogen
(−I is stronger than +M)

1 > 2 > 3 > 4 (−I order)

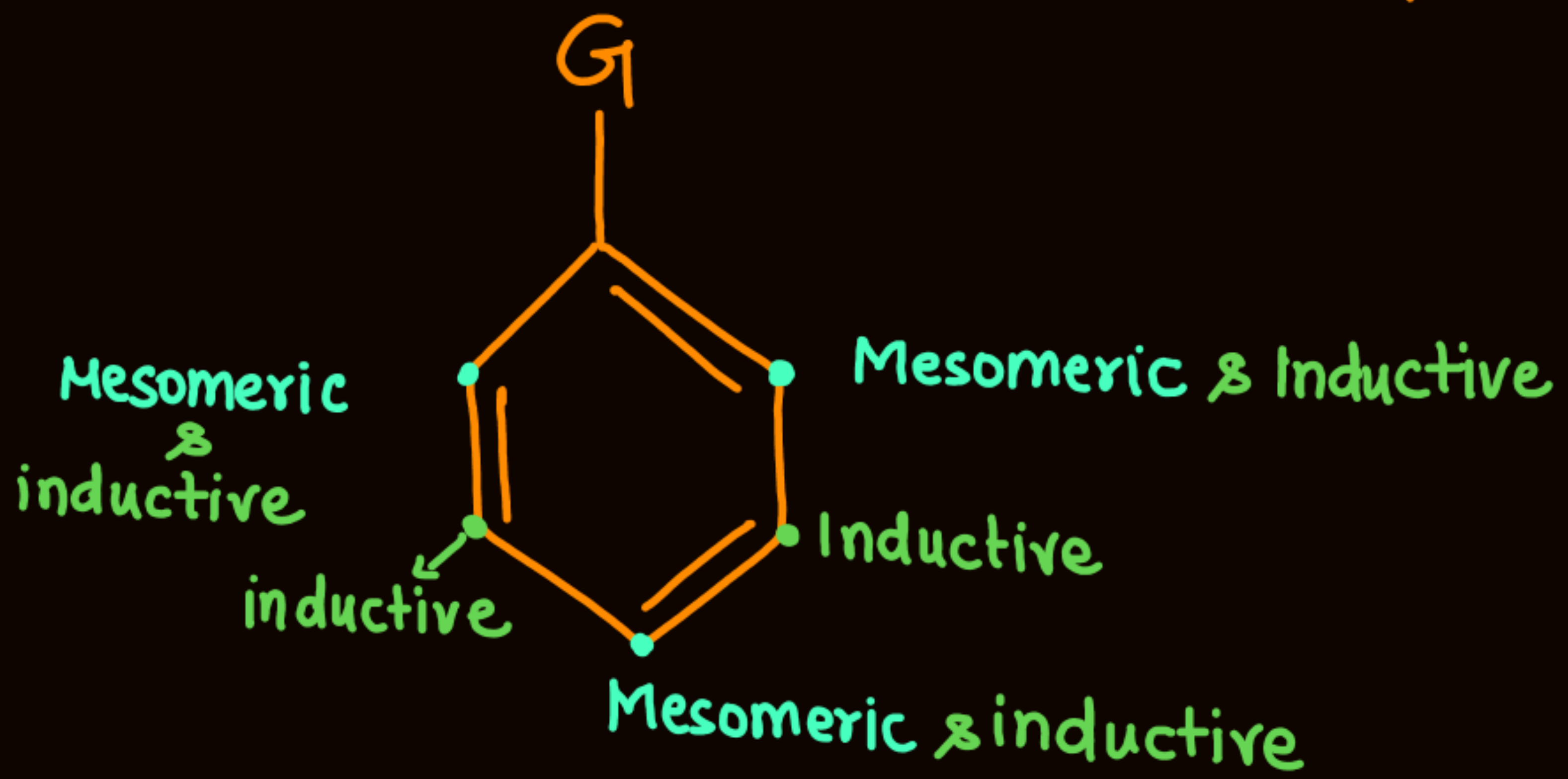
Mesomeric Effect in Benzene Ring





1. +M group increases e^- density at ortho and para.
2. Mesomeric operates only on ortho and para not on meta.
3. Mesomeric at ortho is equal to Mesomeric at para.
4. Mesomeric is distance independent.
5. -M group decreases e^- density at ortho para.

Effects on ortho/Para/Meta



Inductive-ortho > Inductive-meta > Inductive para

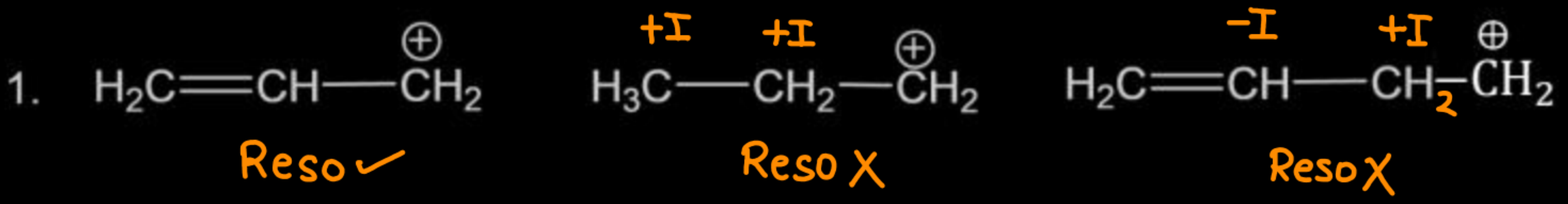
Inductive is distance dependent.

Application of Resonance / Mesomeric Effect

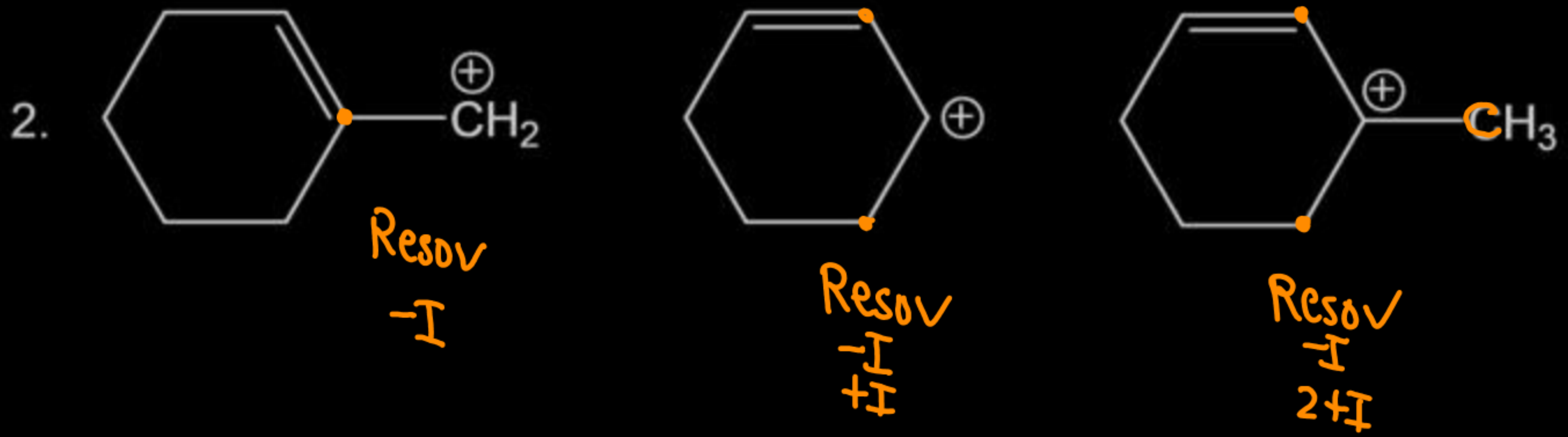
1. Stability of Carbocation (CH_2^+) $\propto +M \propto \frac{1}{-M}$
2. " " Carbanion (CH_2^-) $\propto -M \propto \frac{1}{+M}$
3. " " Free Radical ($CH_2^{\cdot}$) $\propto +M \propto \frac{1}{-M}$
4. Acidic Strength $\propto$ Stab of Carbanion $\propto -M \propto \frac{1}{+M}$
5. Basic Strength $\propto$ Stab of Carbocation $\propto +M \propto \frac{1}{-M}$

Note → Mesomeric effect is Stronger effect than Inductive.

(1) Stability of Carbocation:

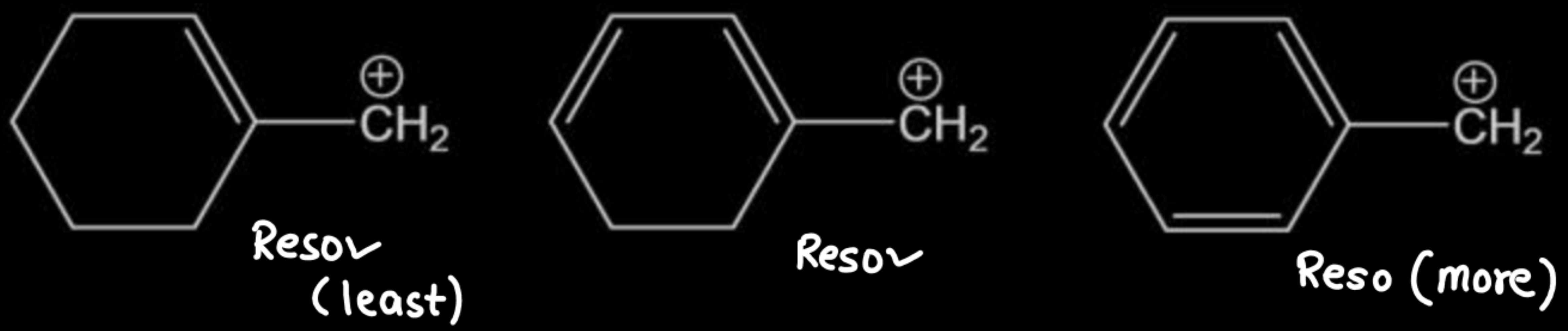


1 > 2 > 3



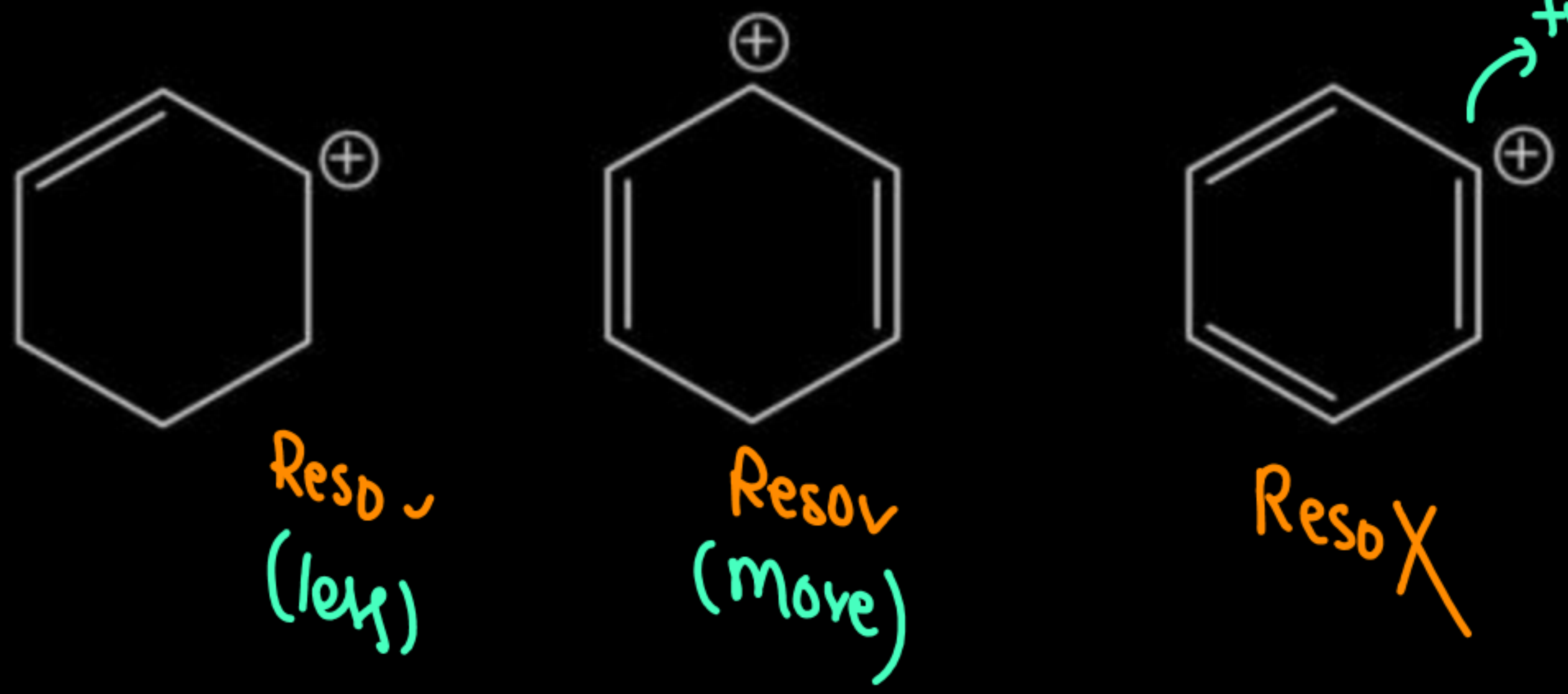
3>2>1

3.



3>2>1

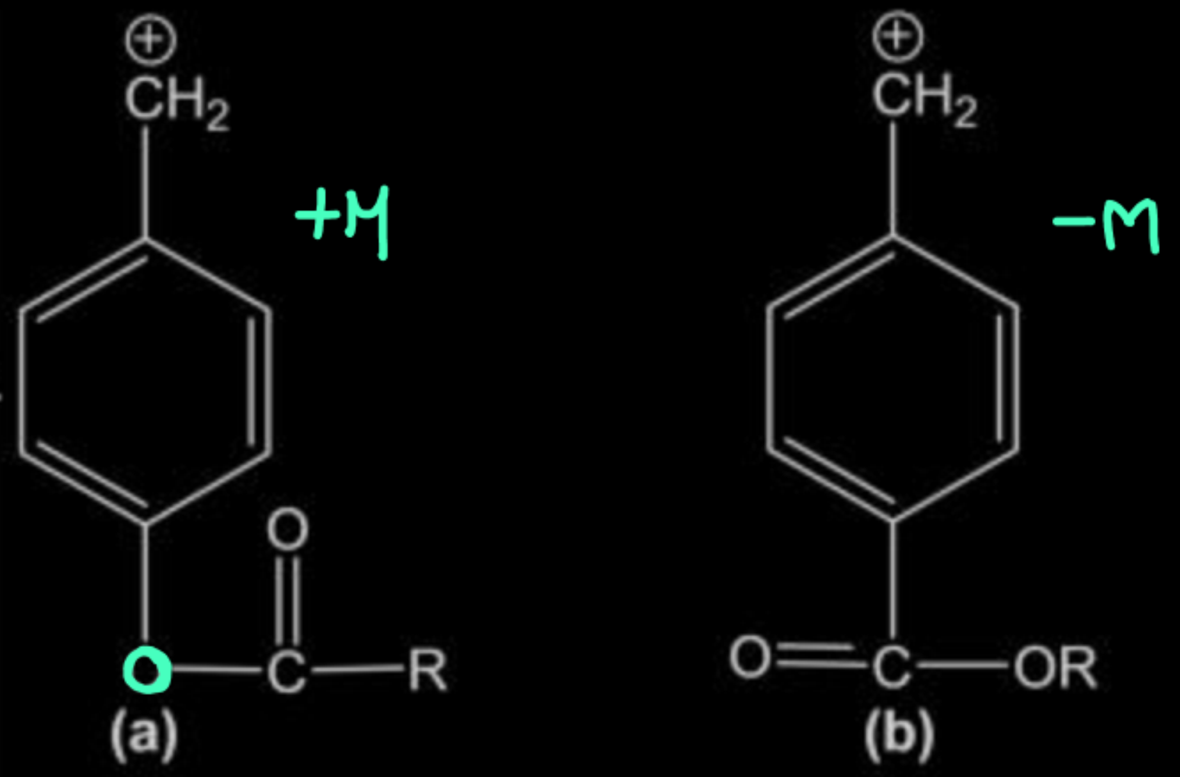
4.



+ve charge on more EN is Unstable.

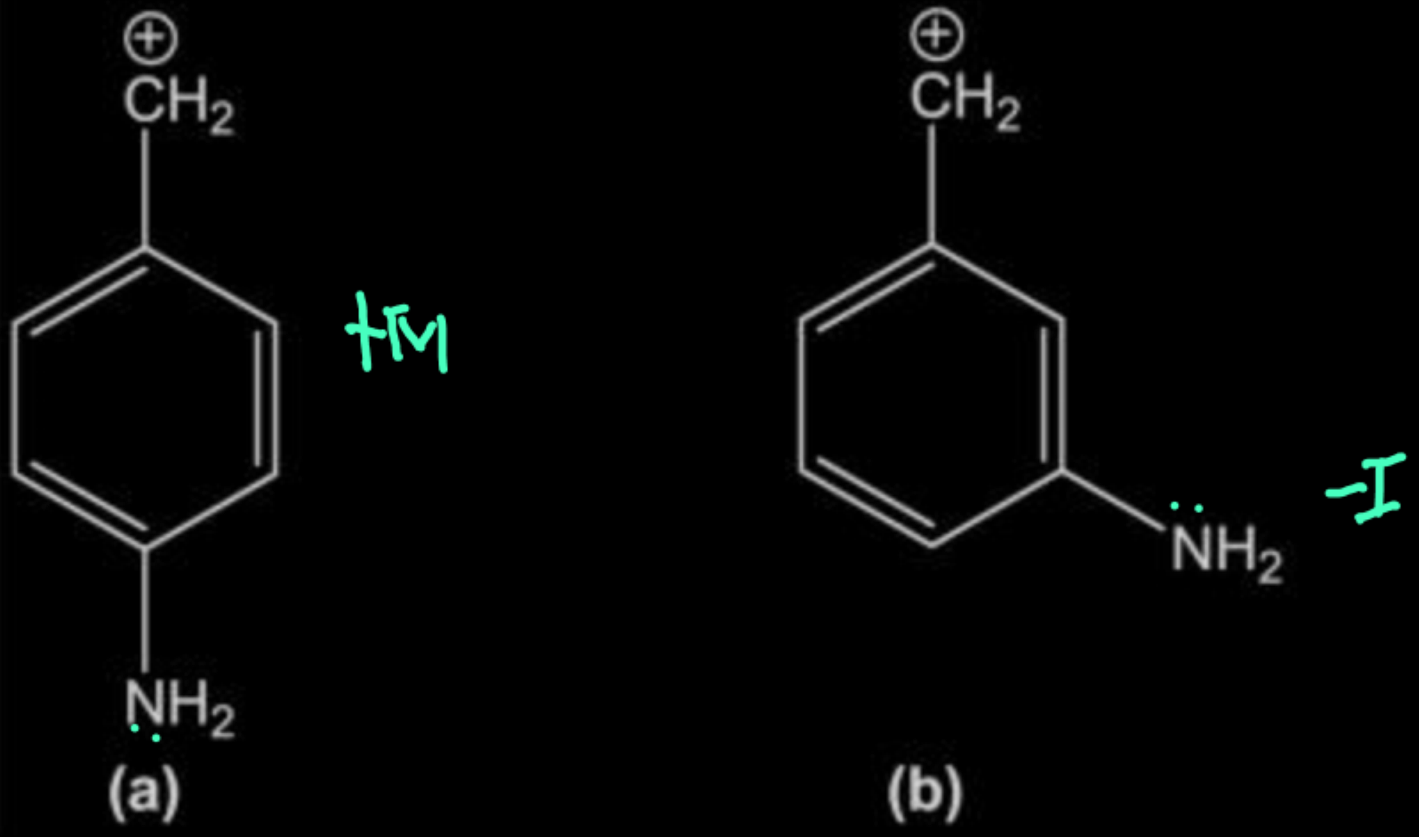
2>1>3

5.



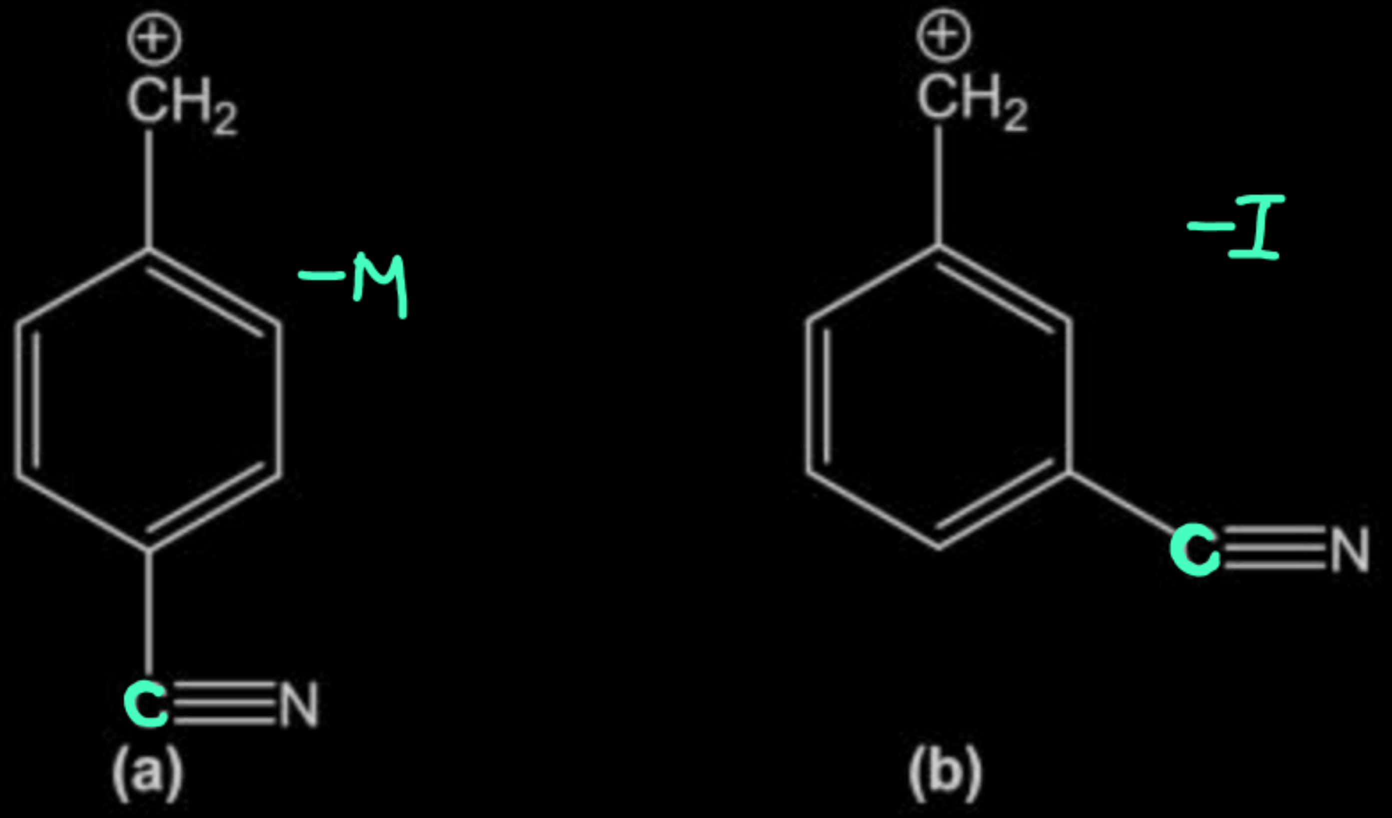
1 > 2

6.



a > b

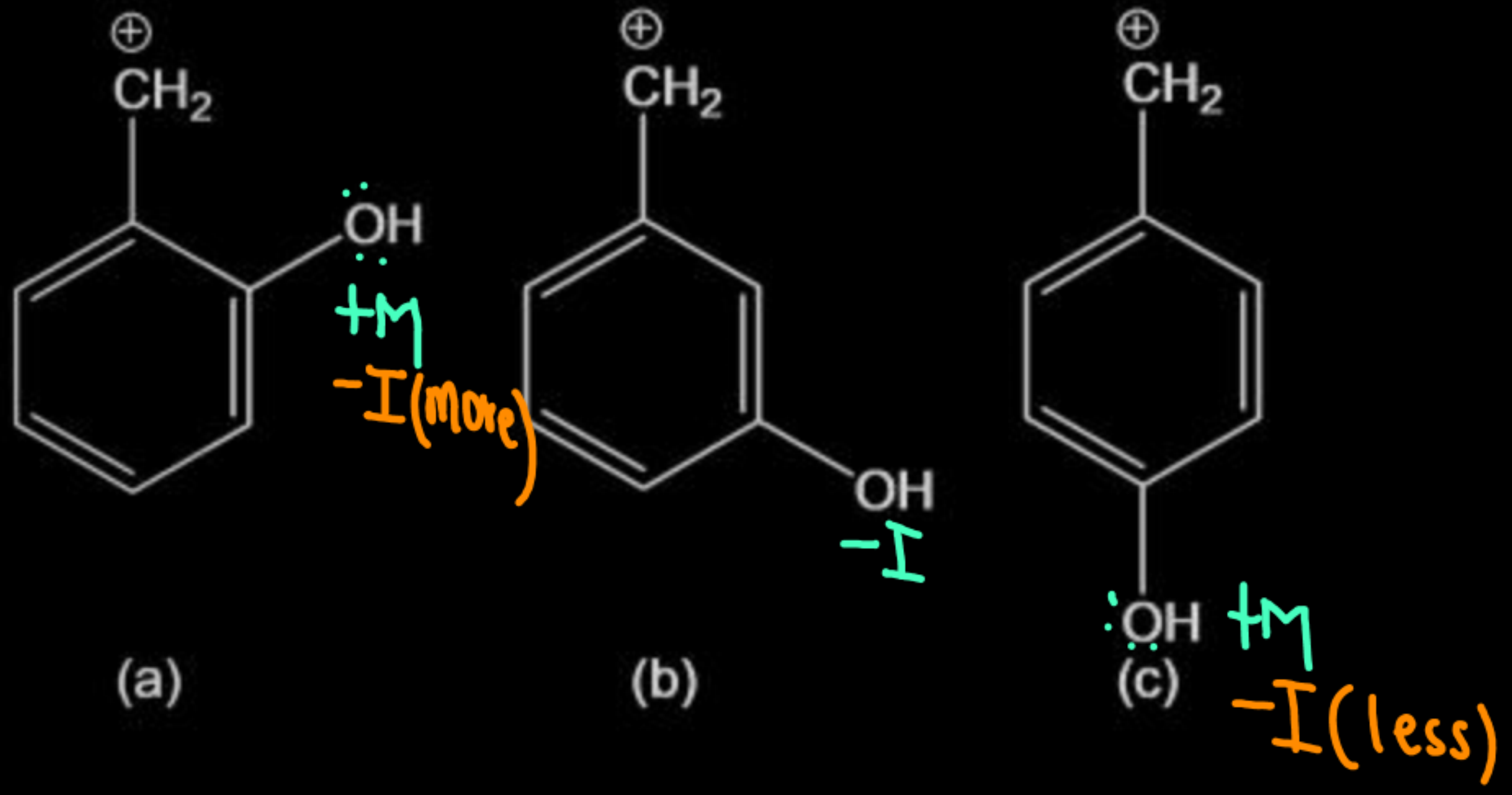
7.



b > a

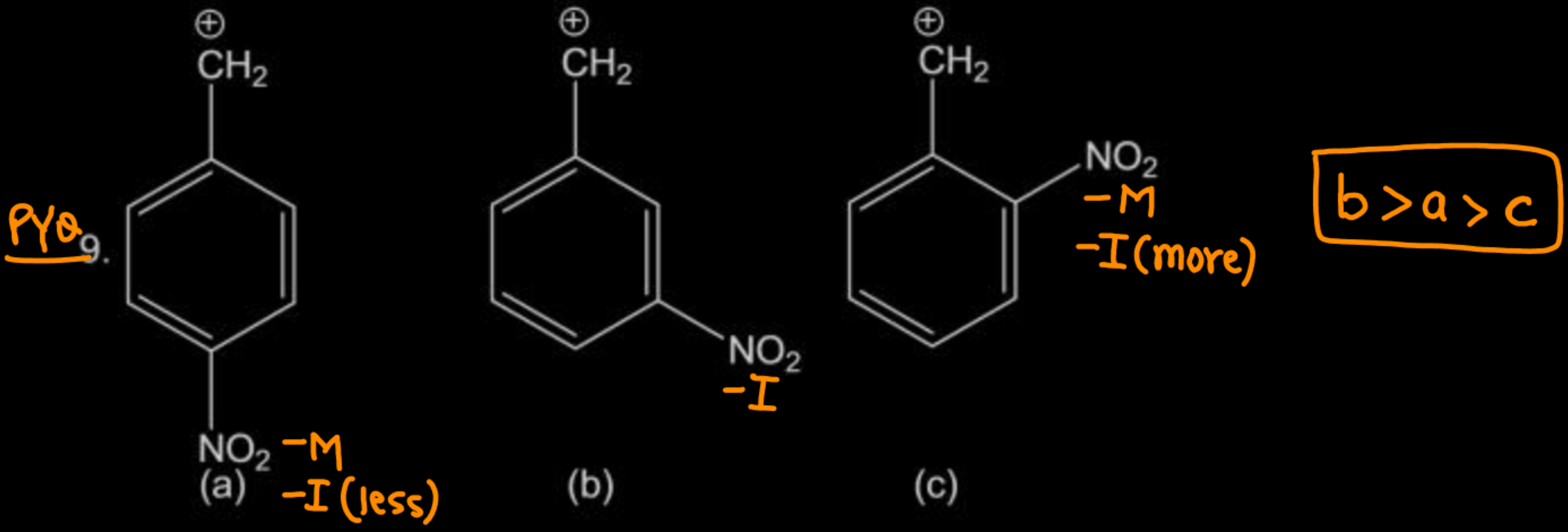
PYQ

8.

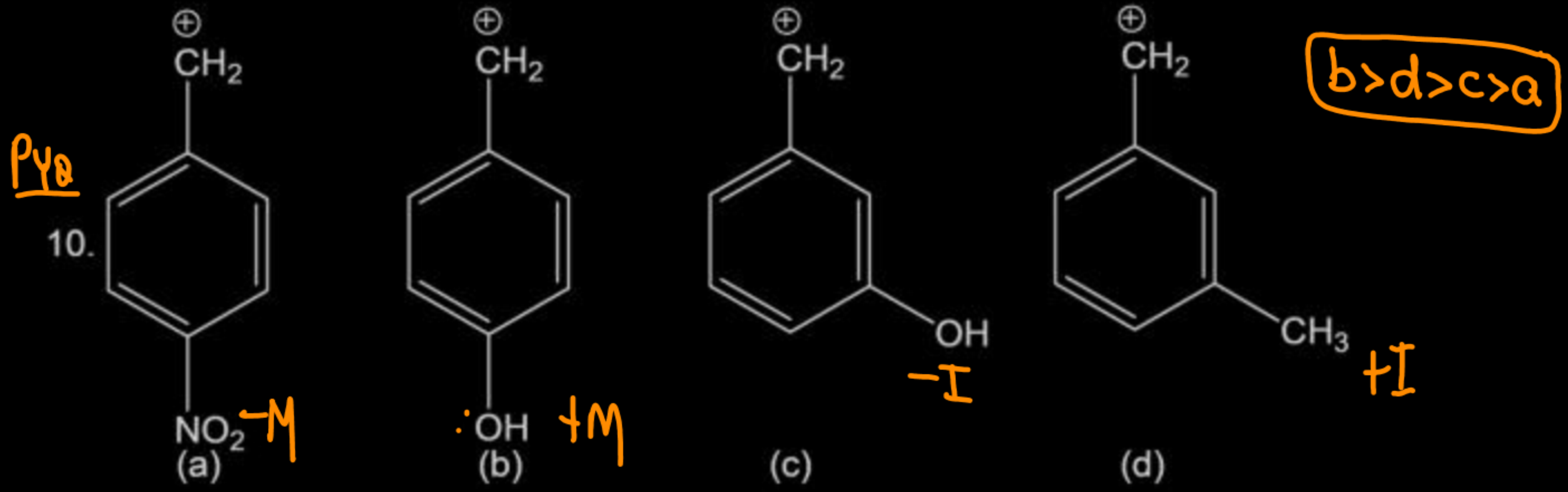


c > a > b

9.


PYQ
CH2
NO2
-M
-I (less)
(a)
(b)
-I
-I(more)
(c)
b > a > c

10.


PYQ
CH2
NO2
-M
(a)
OH
+M
(b)
-I
(c)
CH3
+I
(d)
b>d>c>a

(2) Stability of Carbanion:

–ve charge on more EN

1. $CH_2=CH-\overset{\ominus}{C}H_2$ $\quad$ $CH_2=CH^{\ominus}$ $\quad$ $CH_3-\overset{\ominus}{C}H_2$

Reso ✓ $\quad$ Reso ✗ $\quad$ Reso ✗

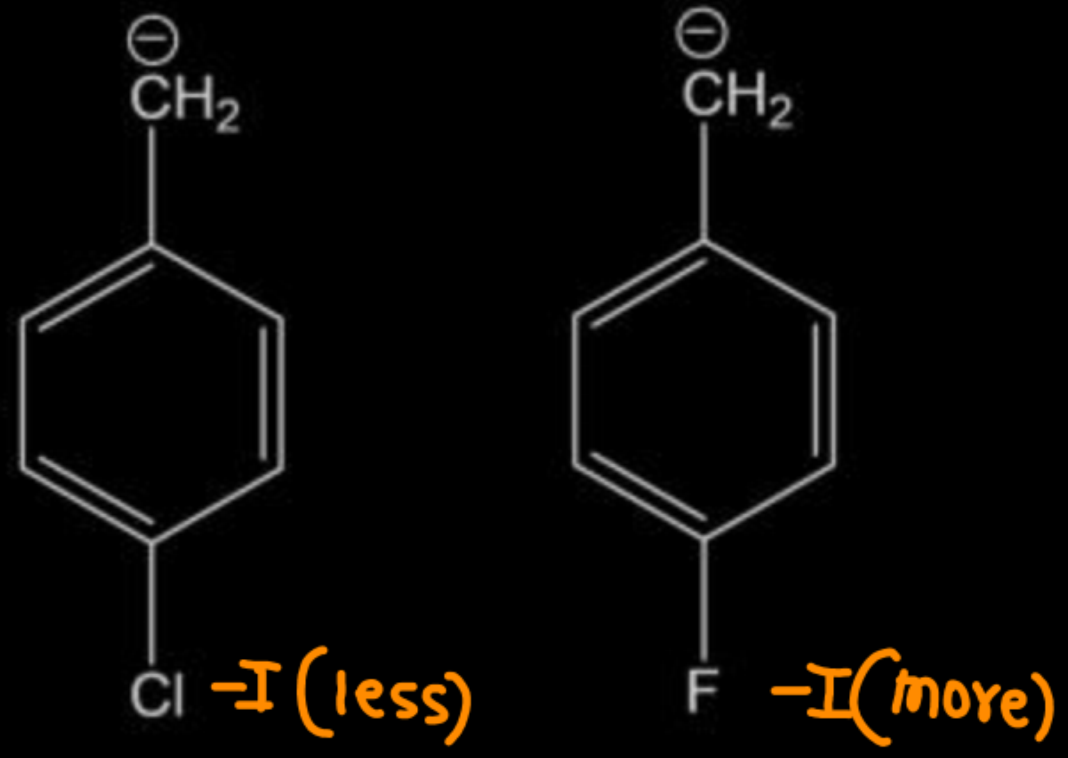
1 > 2 > 3

2. $\overset{\ominus}{C}H_2-NO_2$ $\quad$ $\overset{\ominus}{C}H_2-CH_2-NO_2$ $\quad$ $CH_3-CH^{\ominus}-NO_2$

$\bar{C}H_2-N(=O)\rightarrow O$ $\quad$ Reso ✗ $\quad$ $CH_3-\bar{C}H-N(=O)\rightarrow O$

Reso ✓ $\quad$ **1 > 3 > 2** $\quad$ Reso ✓, +I

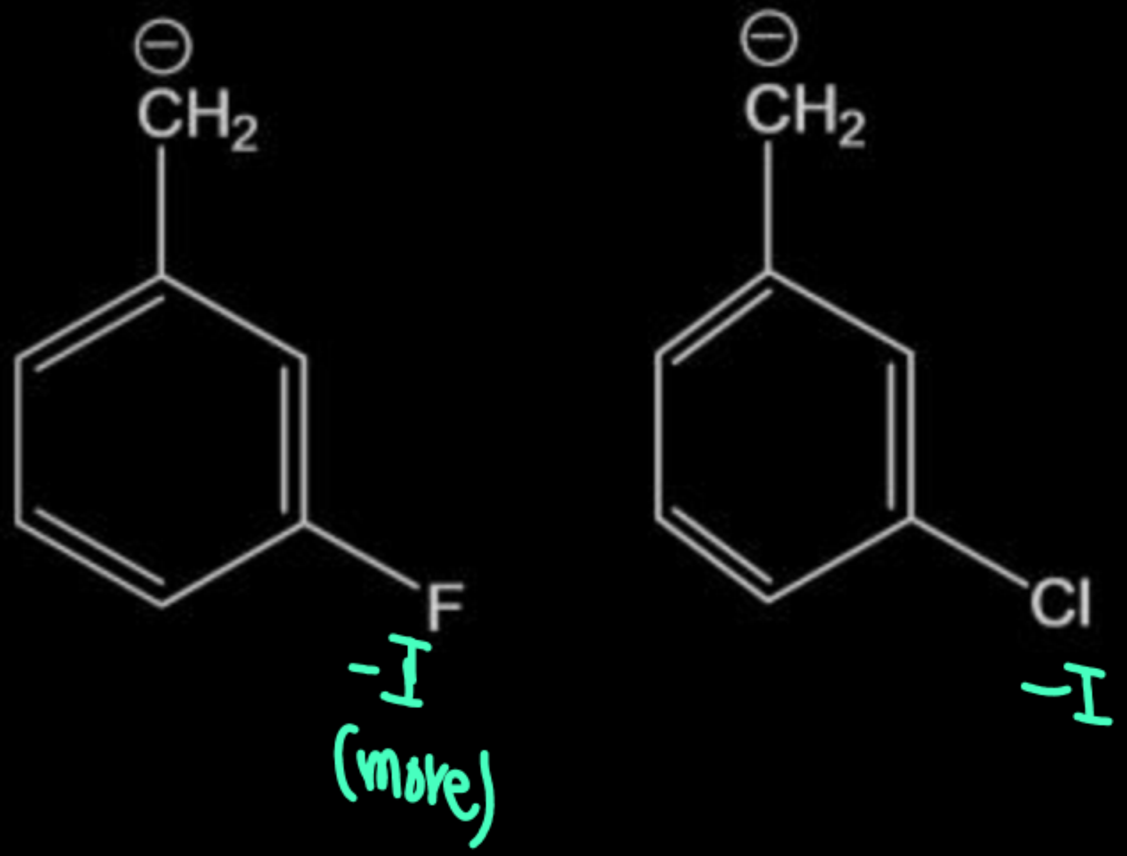
3.



In Halogen → -I is dominating factor.

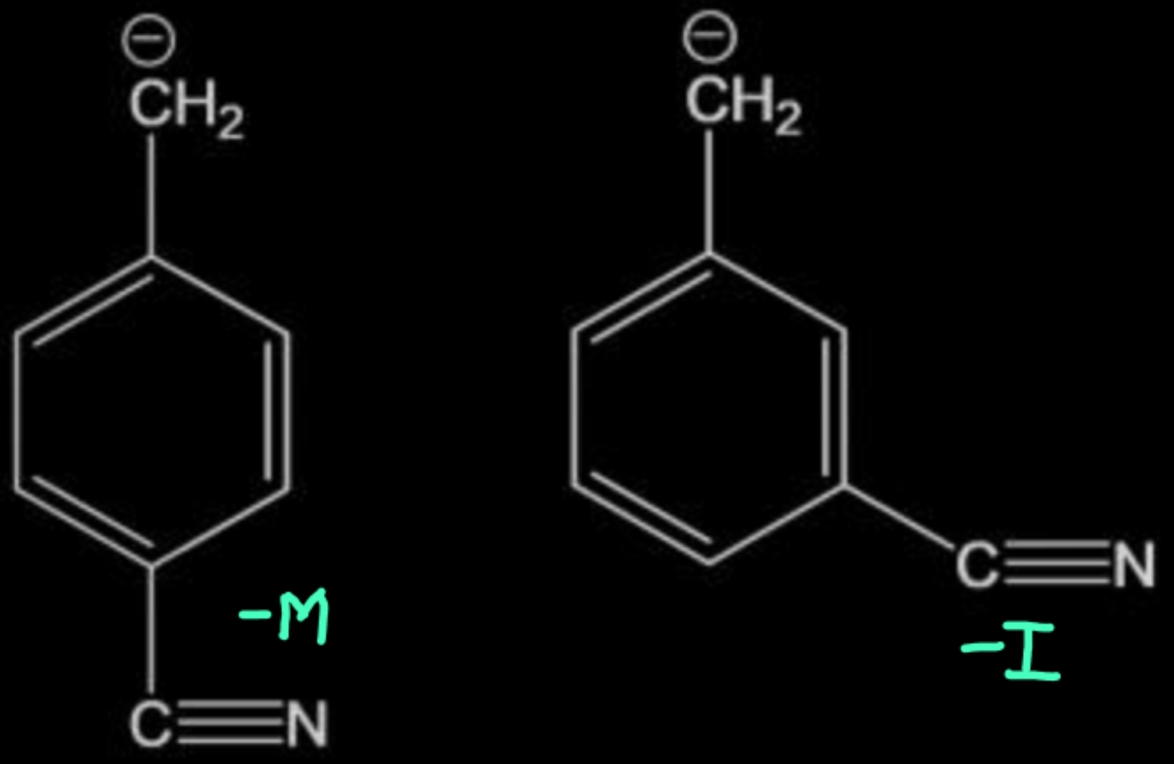
b>a

4.



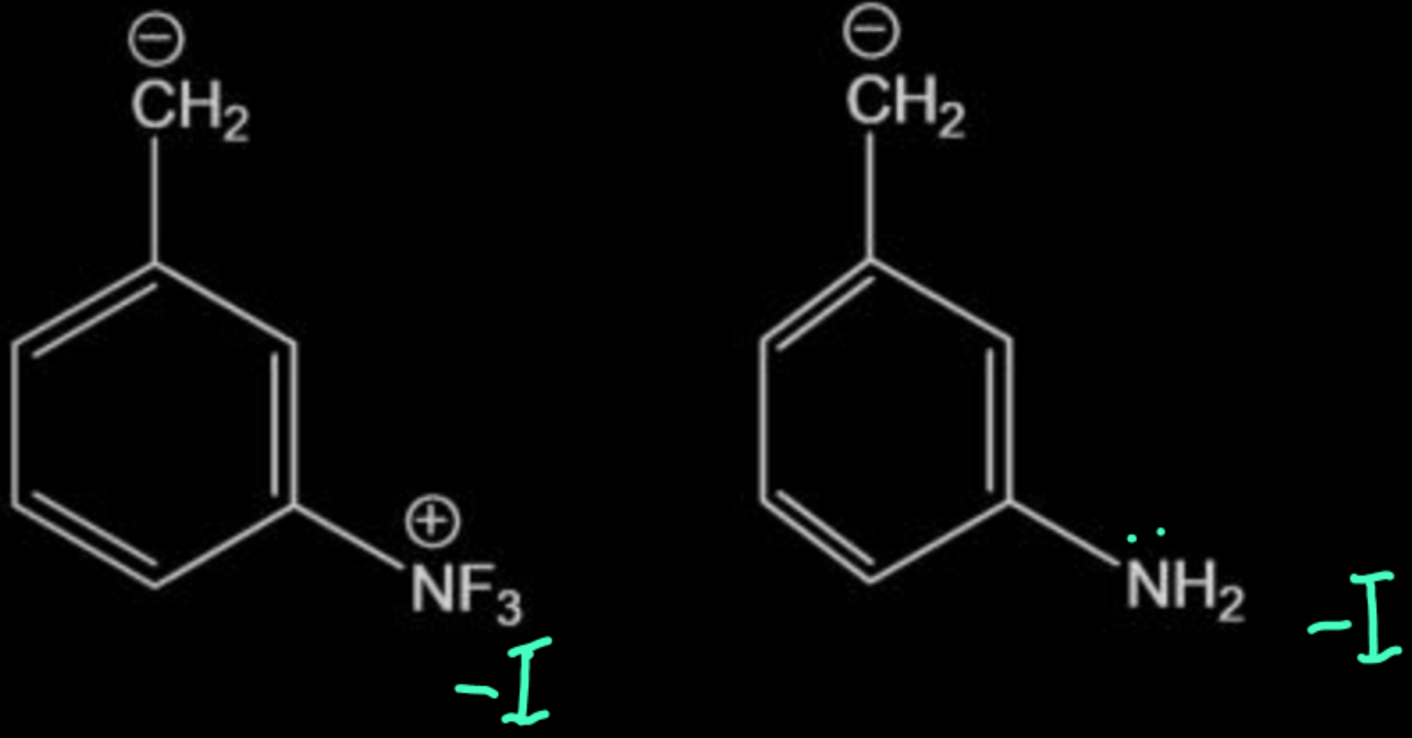
a>b

5.



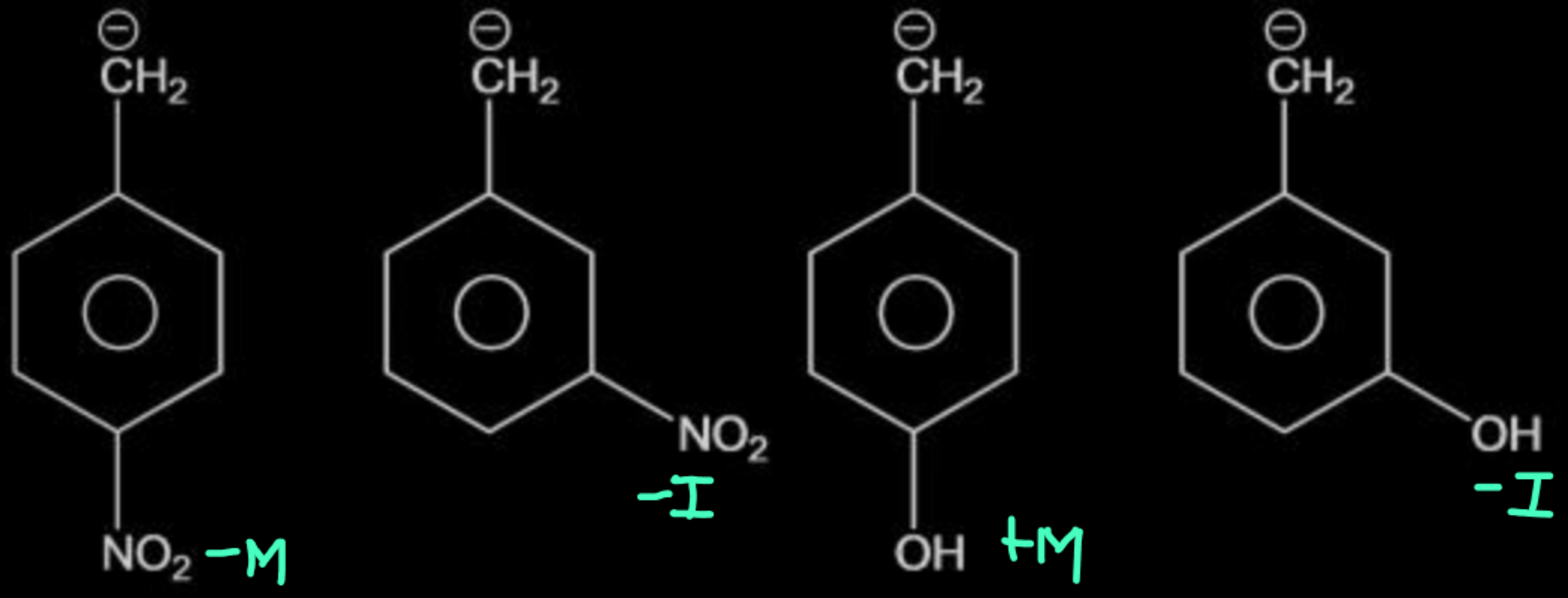
a > b

6.



a > b

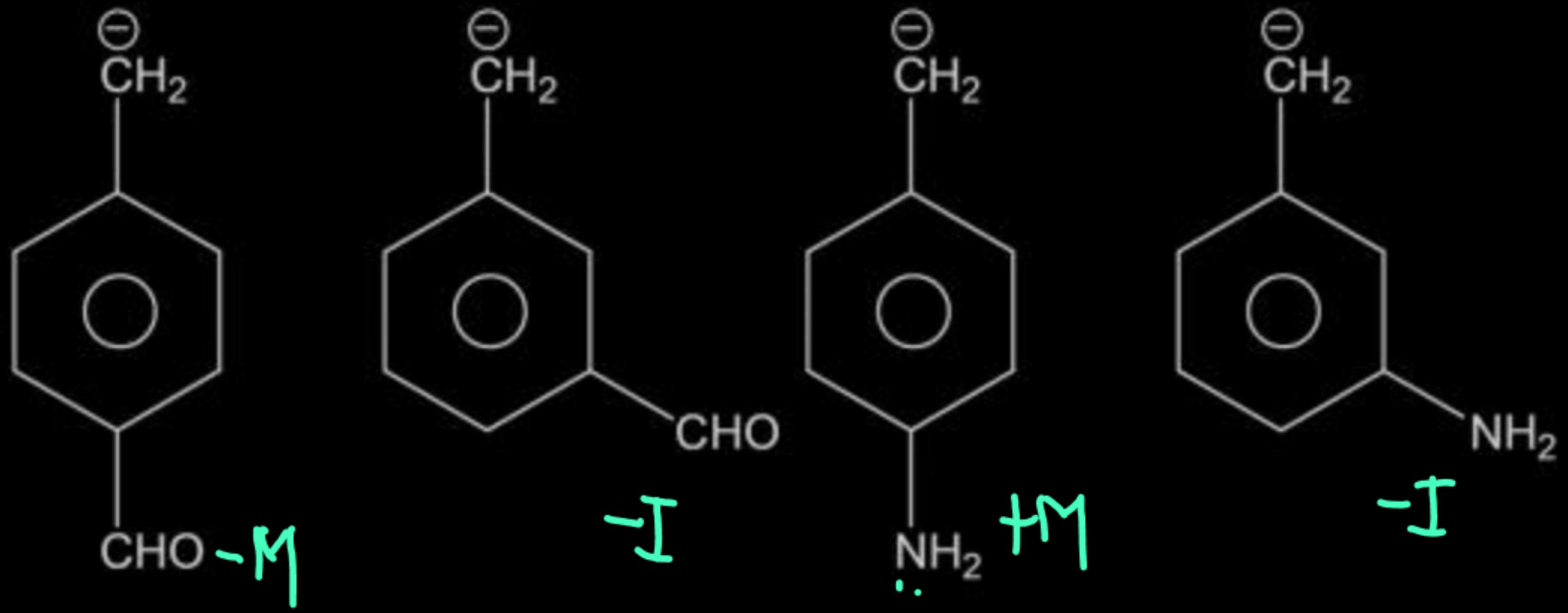
7.



CH₂
NO₂ −M
CH₂
NO₂
−I
CH₂
OH +M
CH₂
OH
−I

a > b > d > c

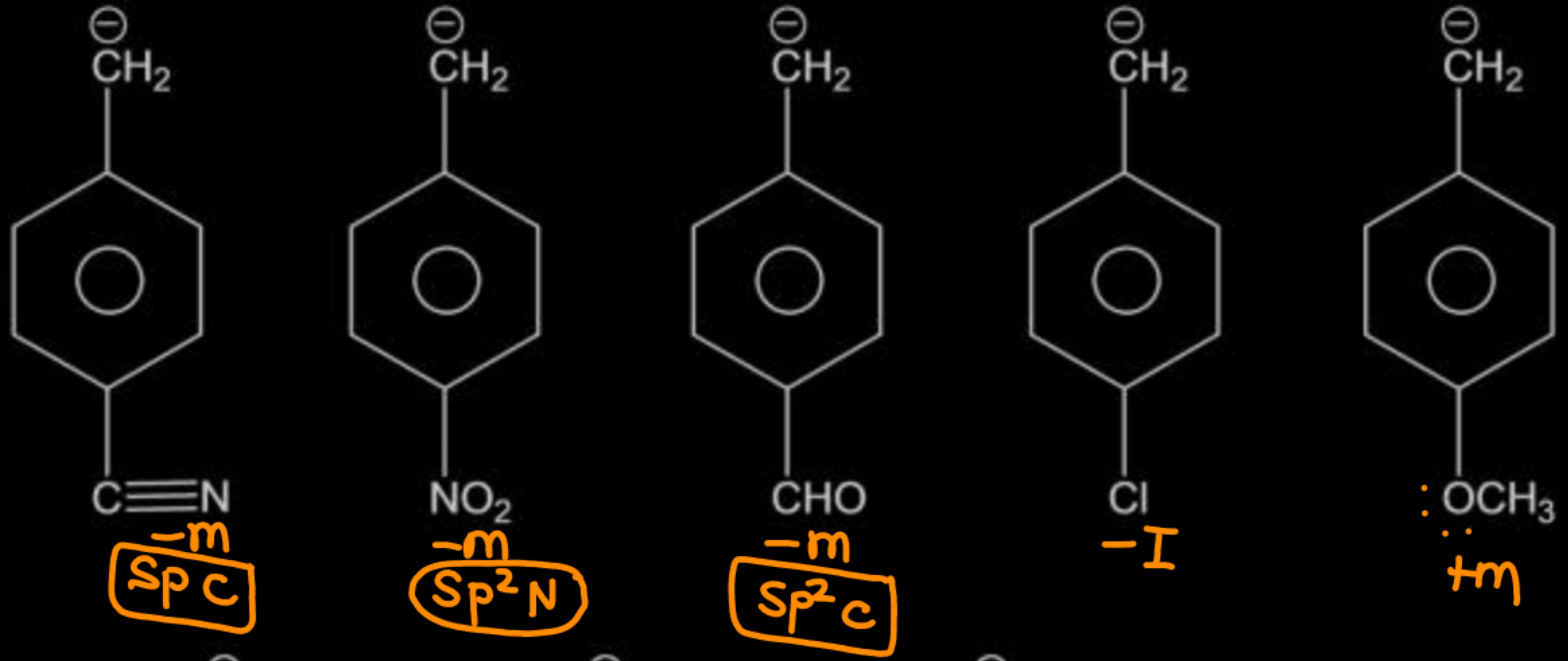
8.



CH₂
CHO −M
CH₂
CHO
−I
CH₂
NH₂ +M
CH₂
NH₂
−I

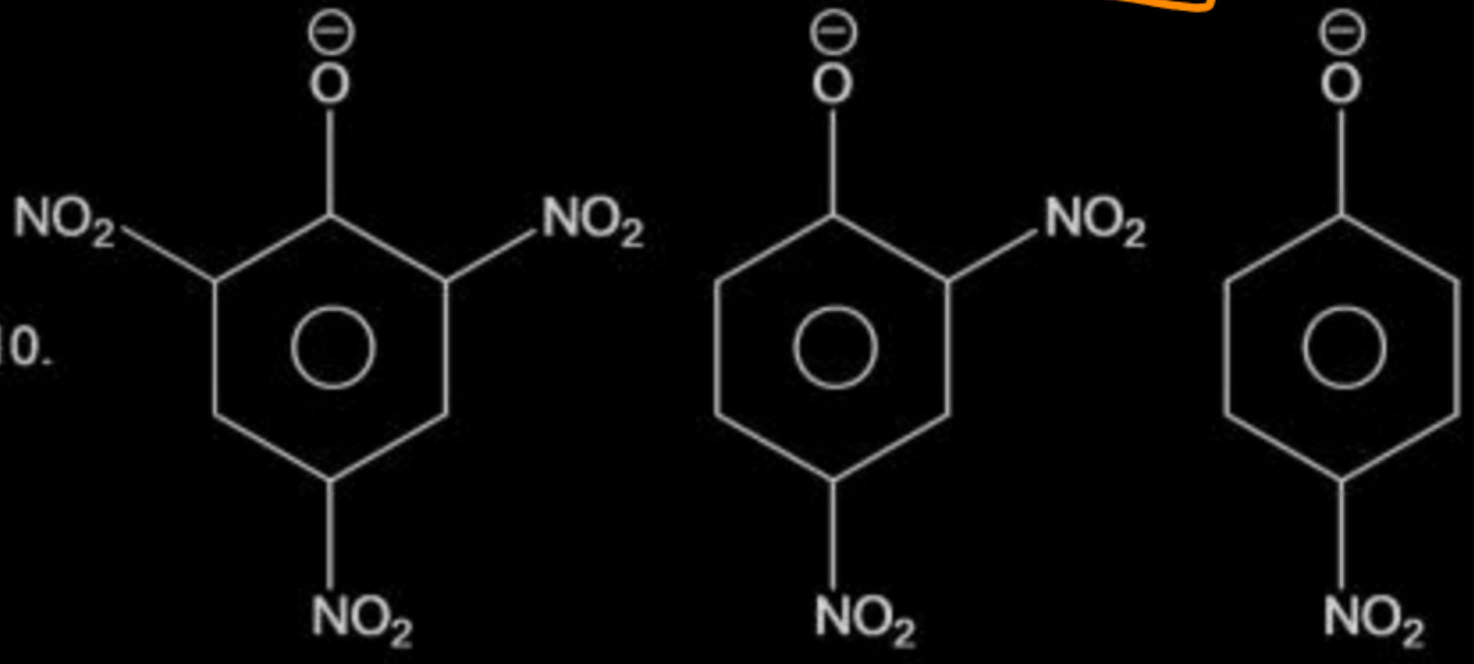
a > b > d > c

9.

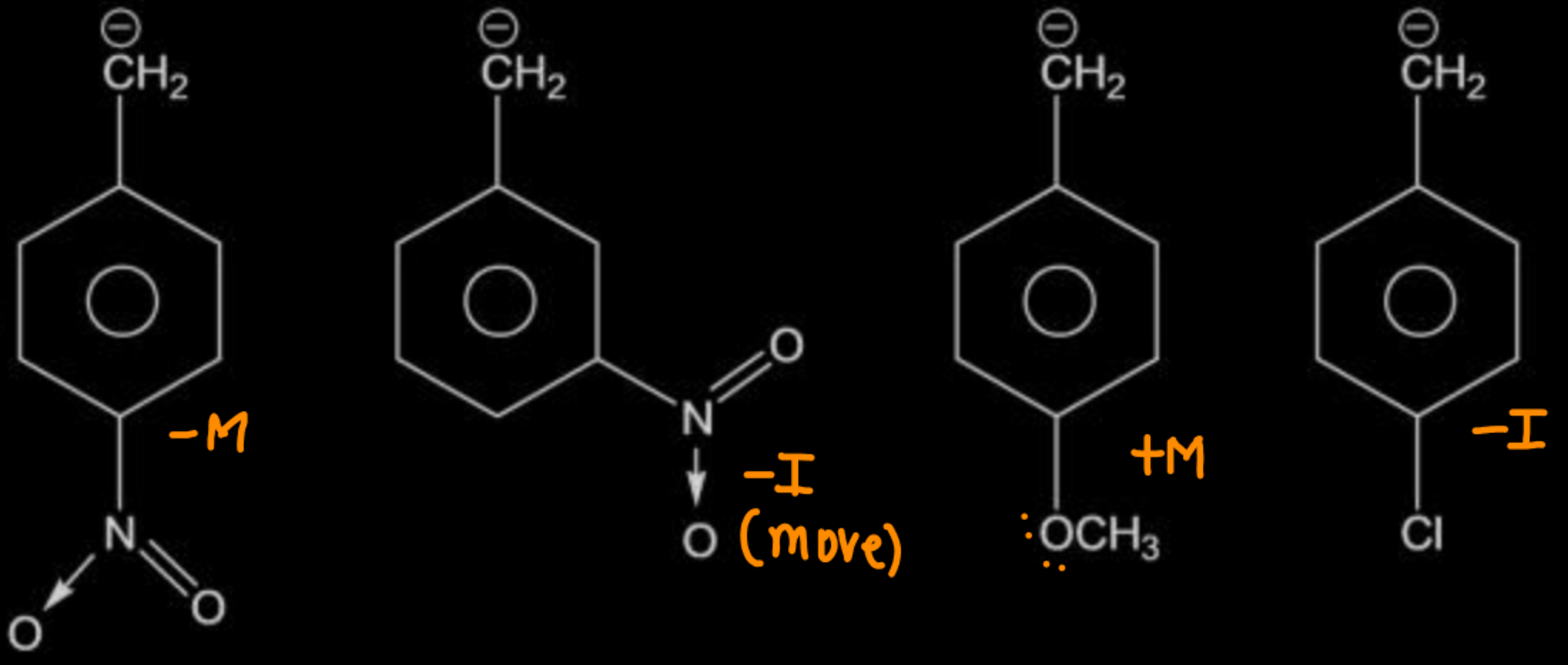


b>a>c>d>e

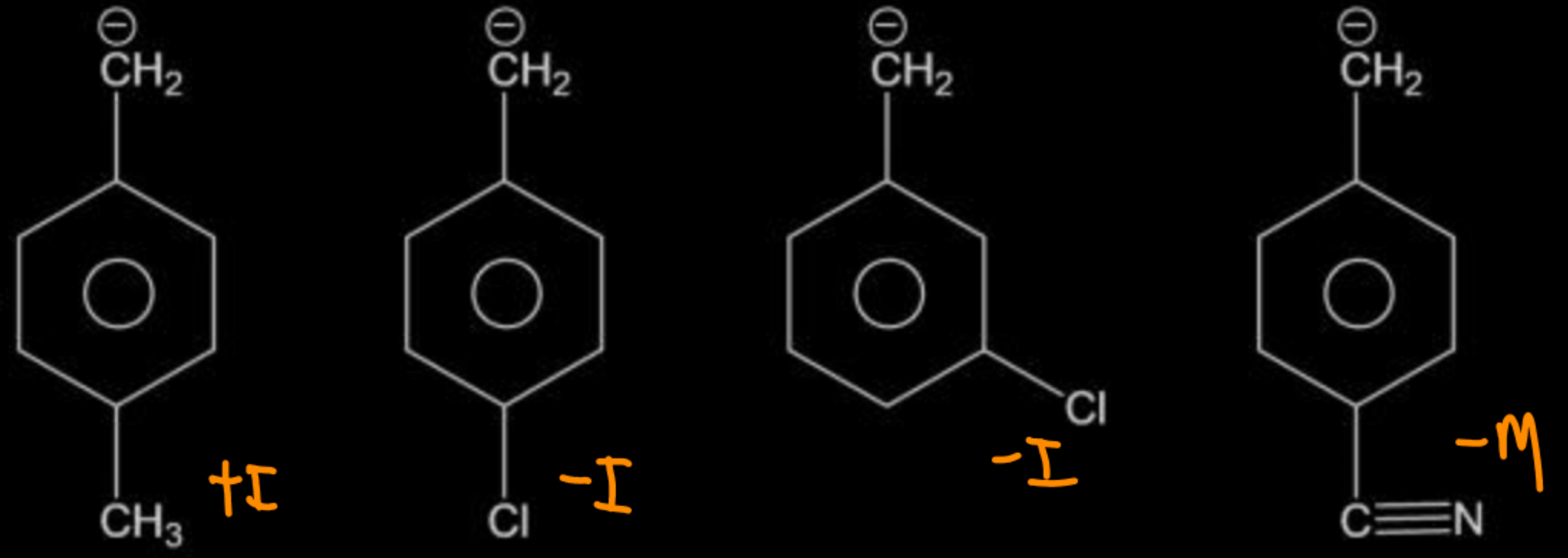
10.



1>2>3

11. 

a > b > d > c

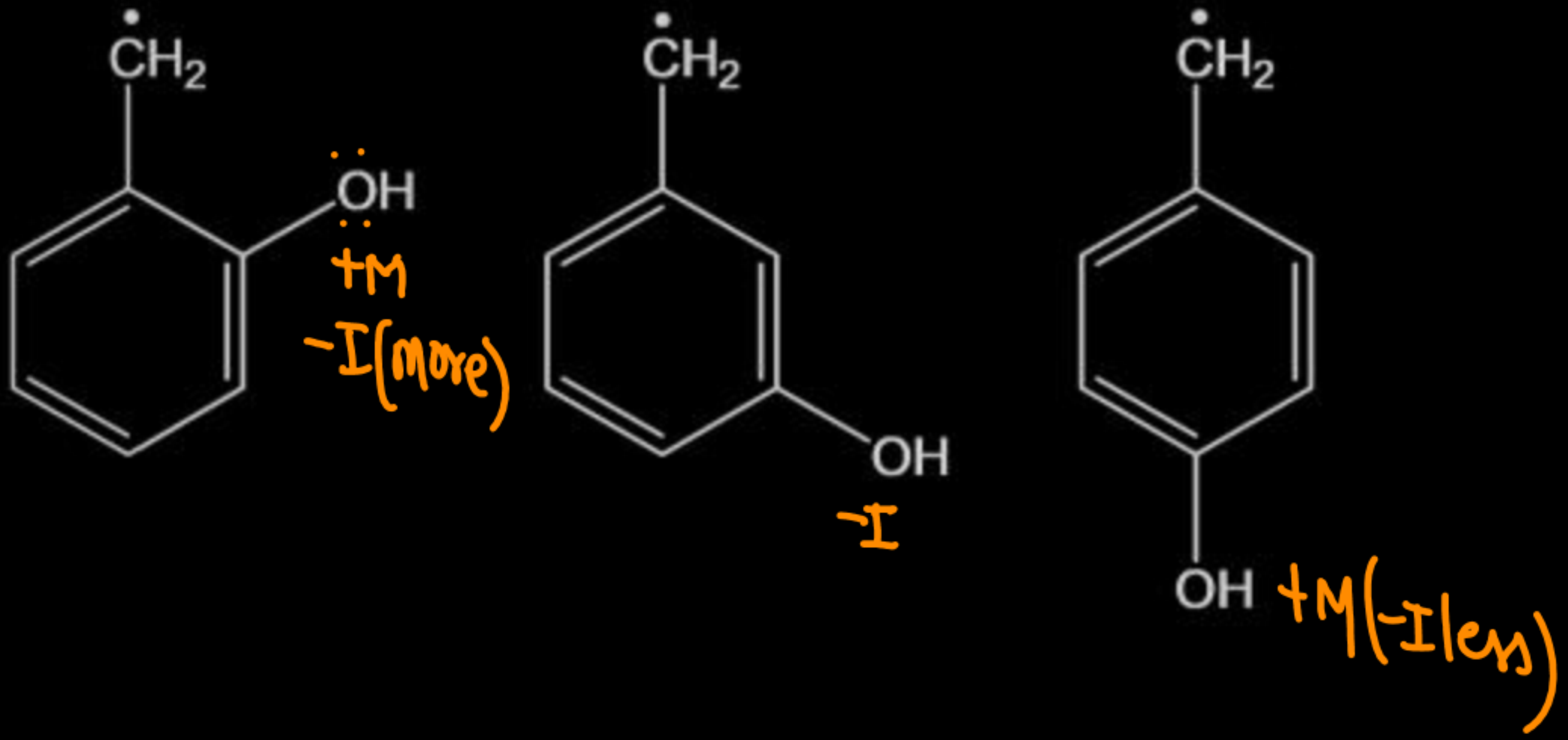
12. 

d > c > b > a

13. 

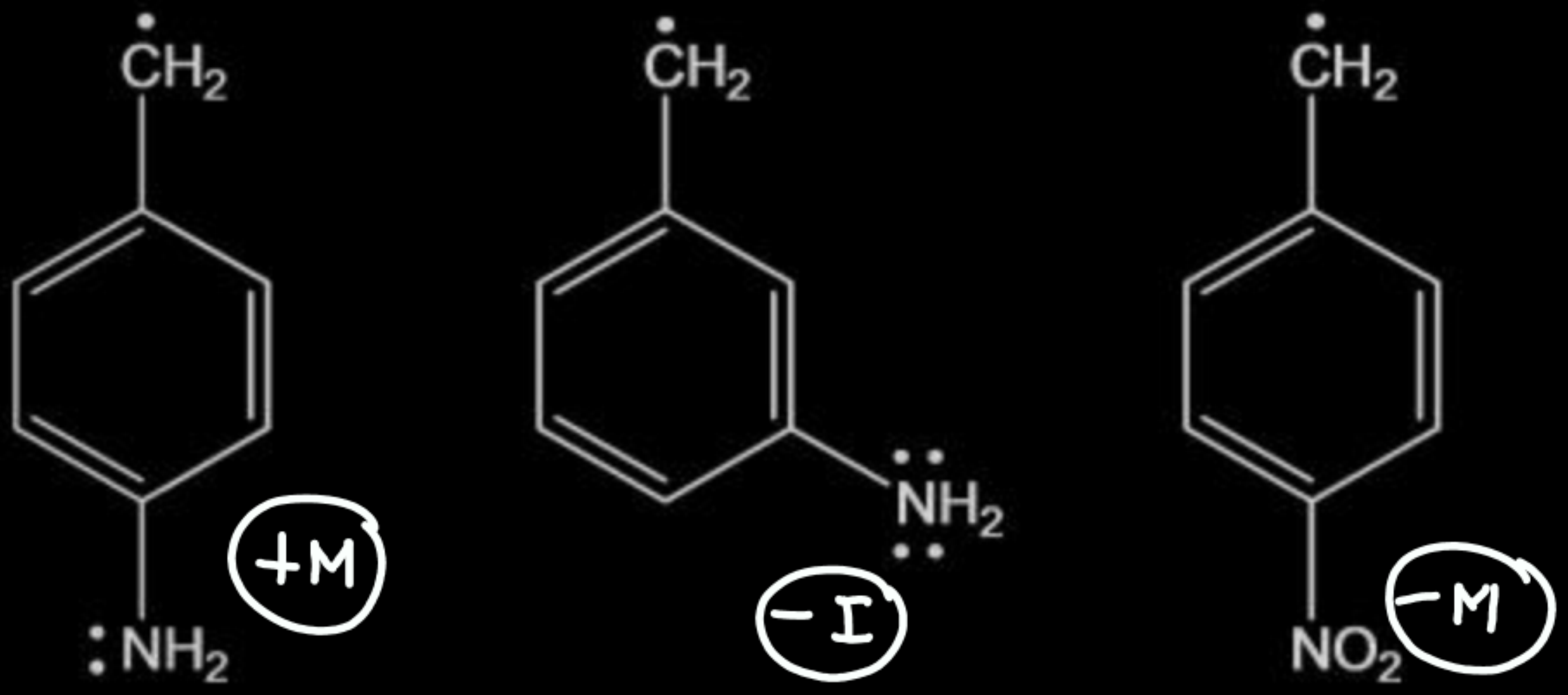
note → Free Radical / +ve charge is Unstable on more EN.

b > a > c

14. 

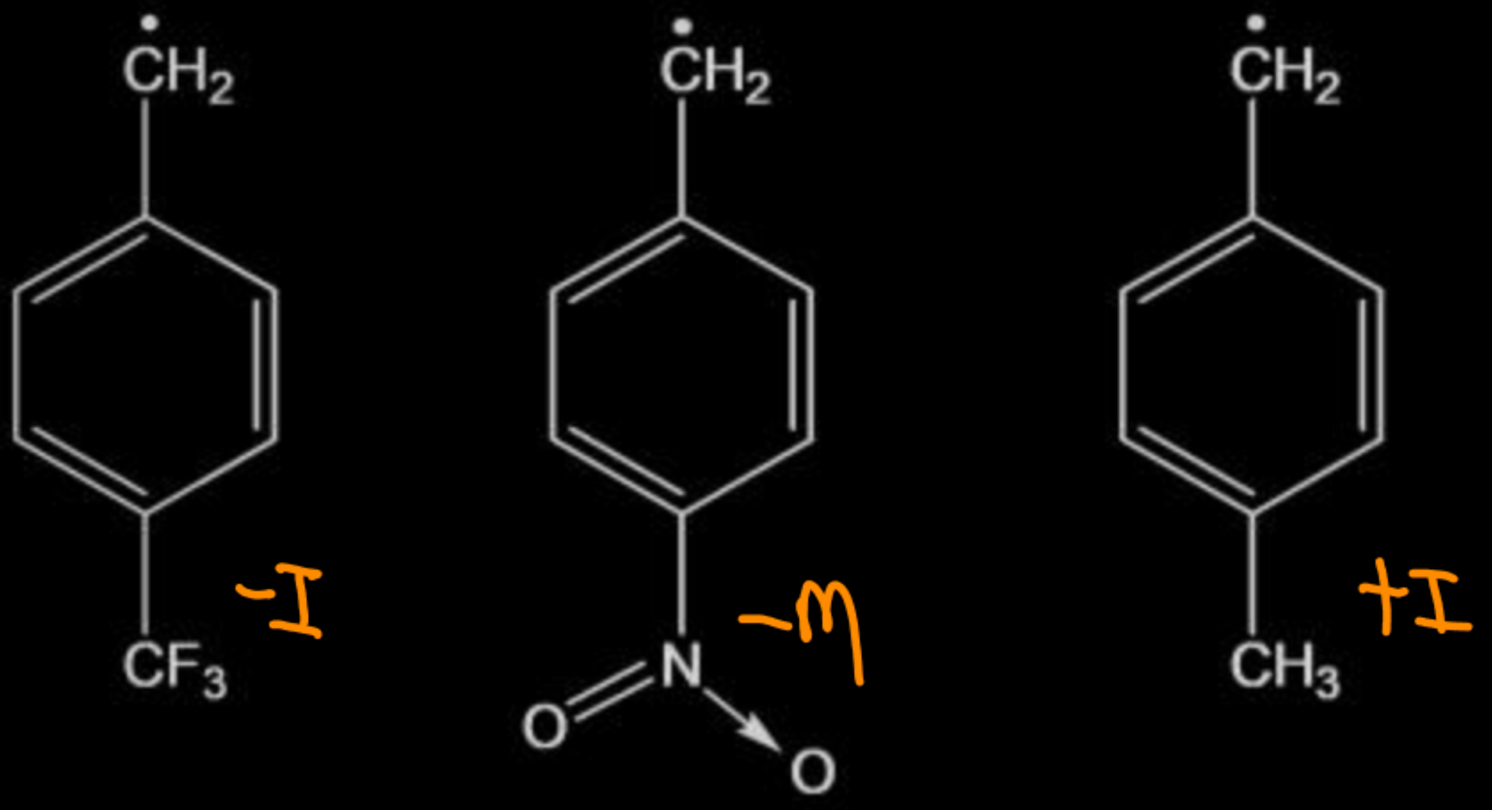
c > a > b

15.



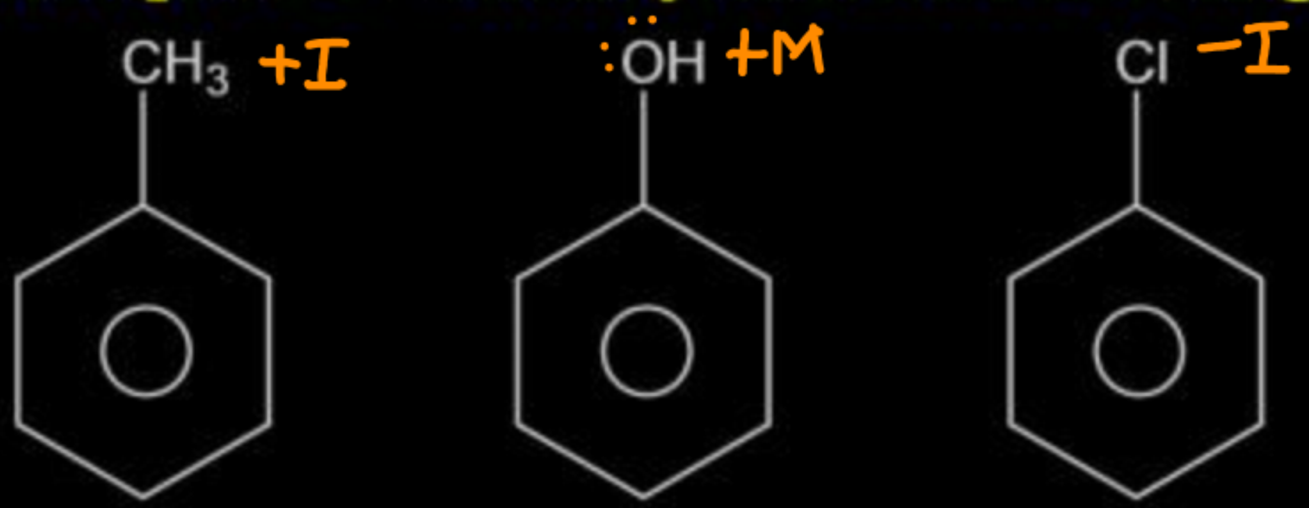
a > b > c

16.

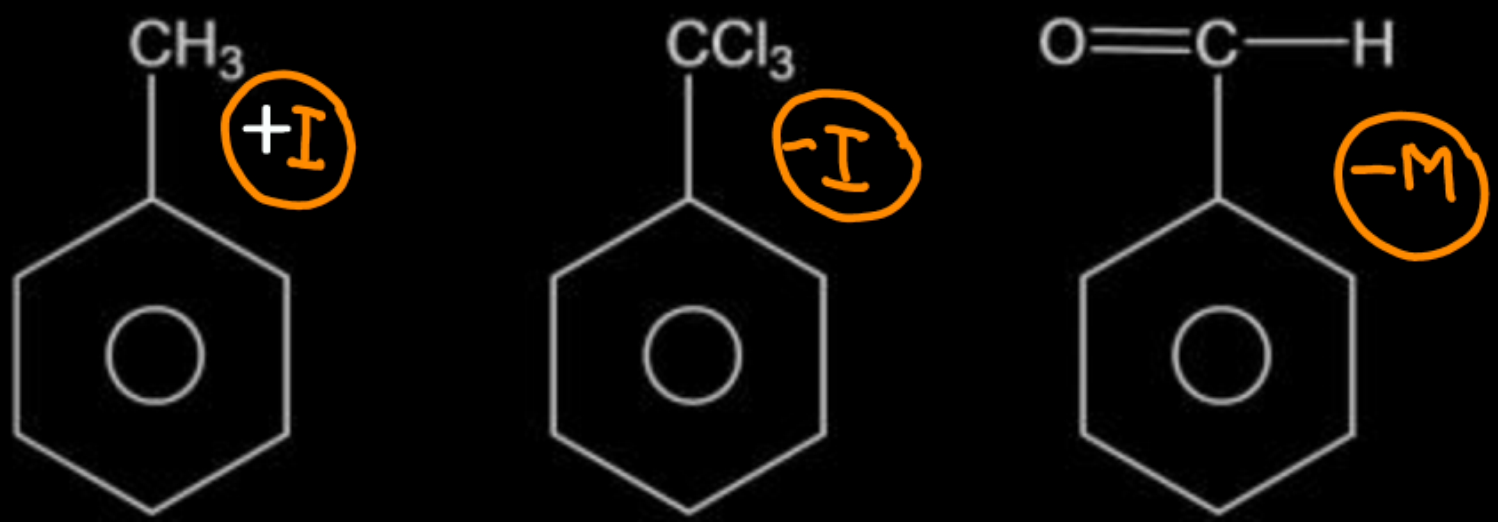


c > a > b

Q. Compare e⁻ density on Benzene Ring:

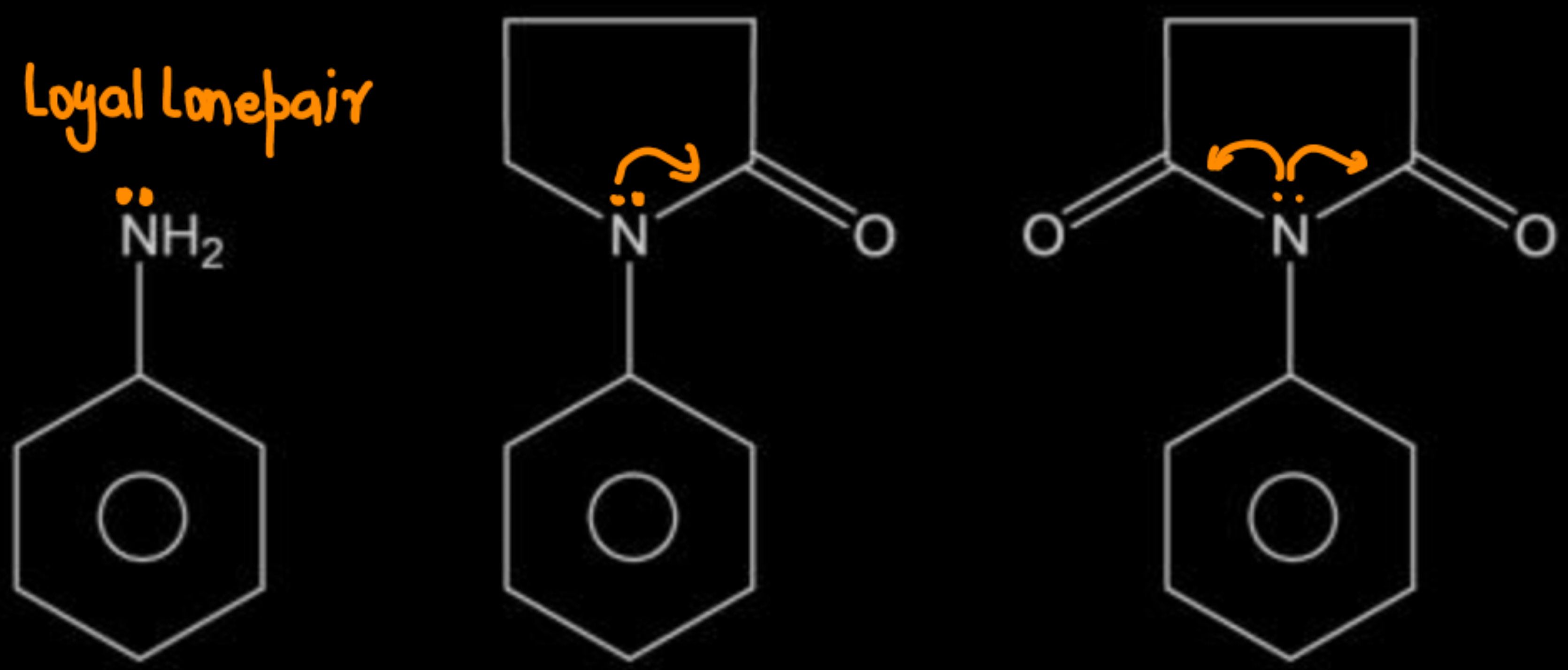
1. 

b > a > c

2. 

a > b > c

3.



a > b > c

① Acidic Strength $\propto -M \propto \frac{1}{+M}$

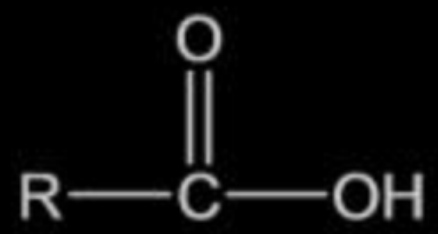
② Equivalent RS is more stable than normal Resonating str.



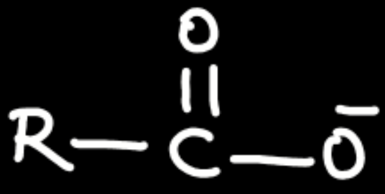
(Equivalent Rs)
(Symmetry)

*** Acidic Strength:**

1.







>



Equivelent R-S

normal R·S

1>2

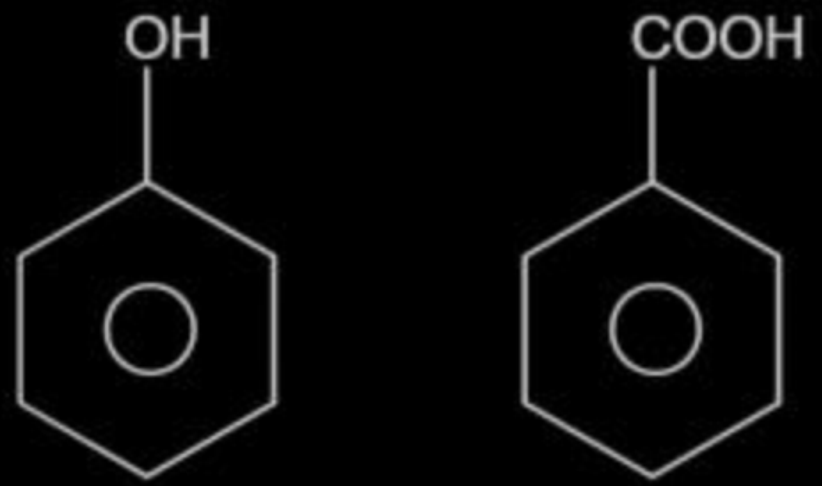
2. Ph—OH   R—OH

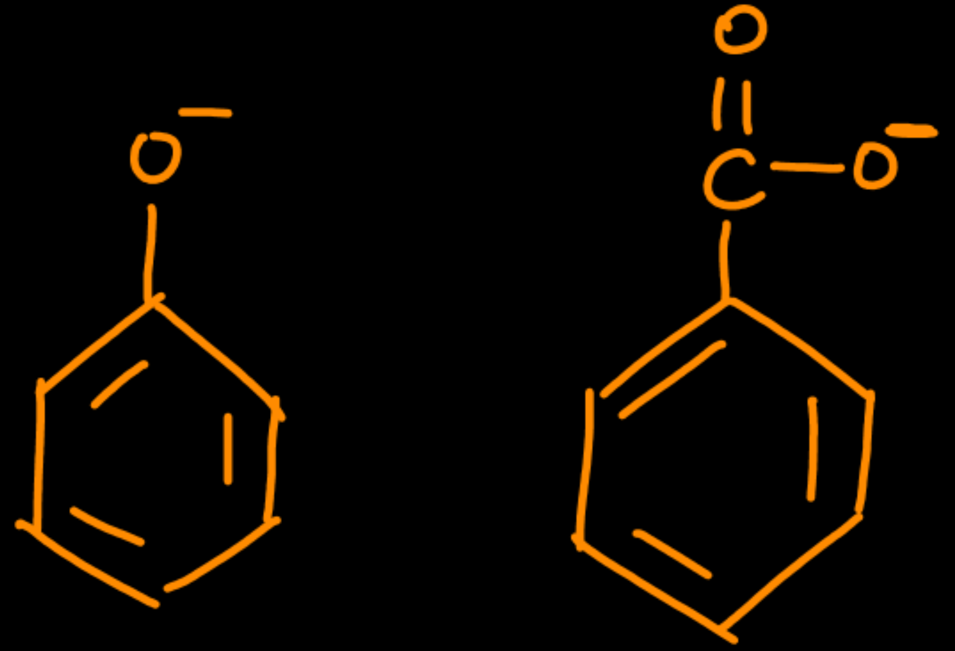


$R-O^-$

Reso ✓   Reso ✗

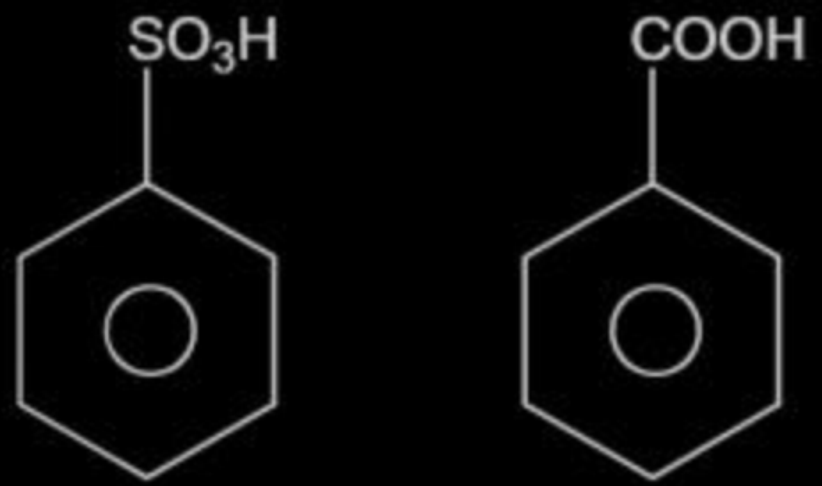
1>2

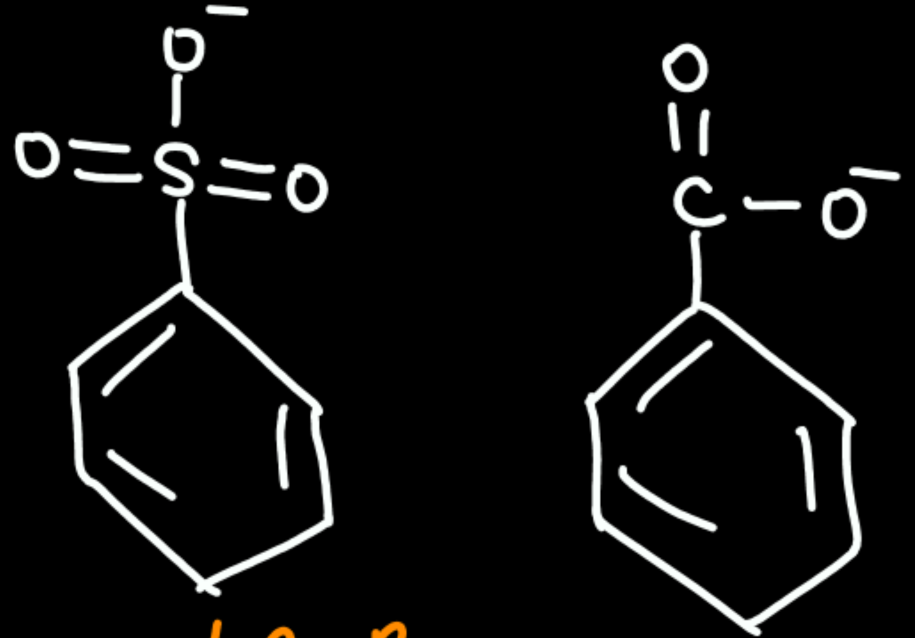
3. 



Equivalent RS

2>1

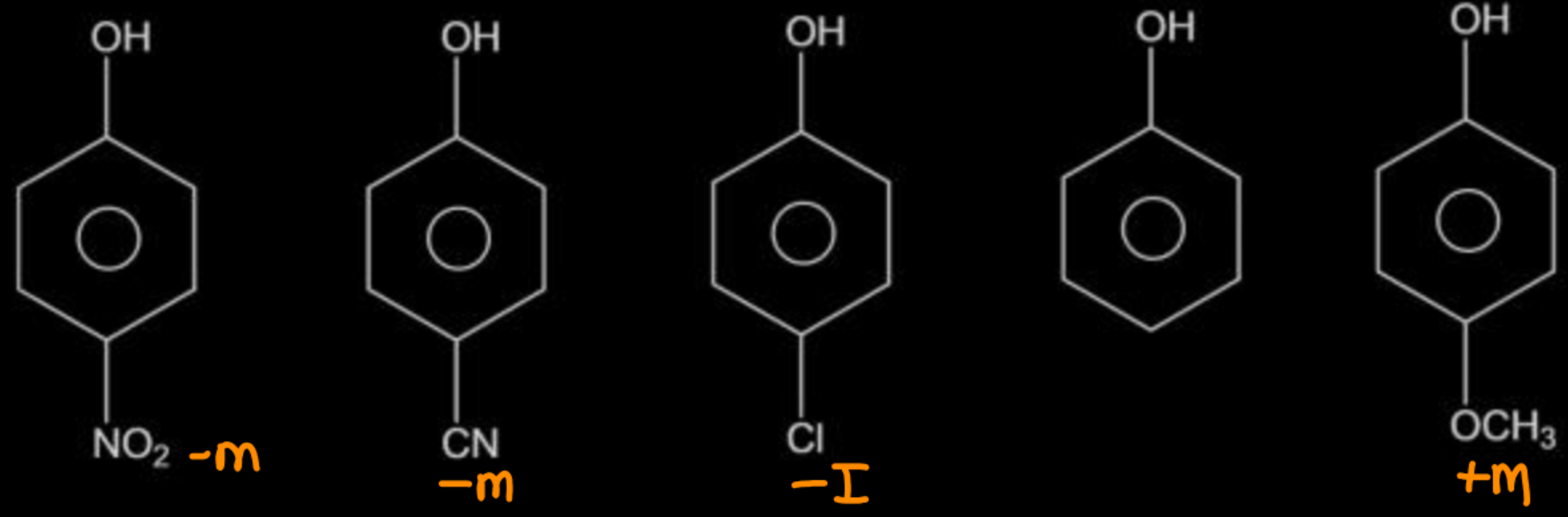
4. 



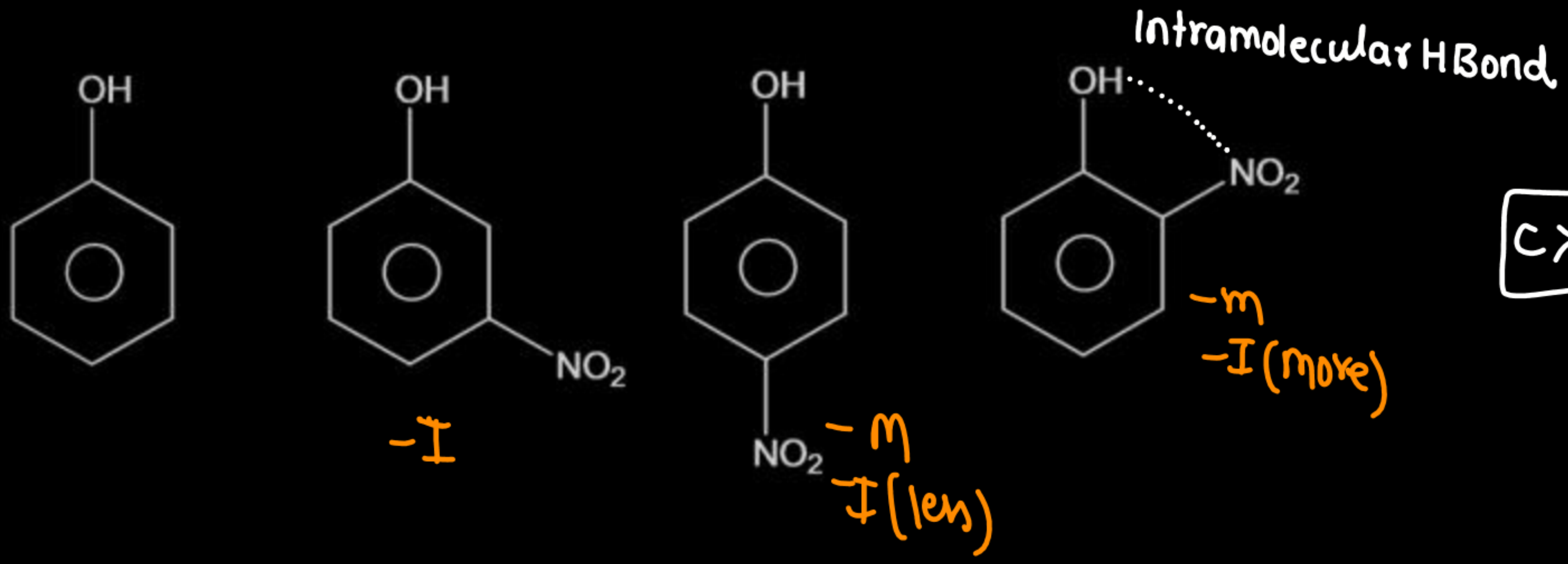
Eq^t Reso (more)

Eq^t Reso

a>b

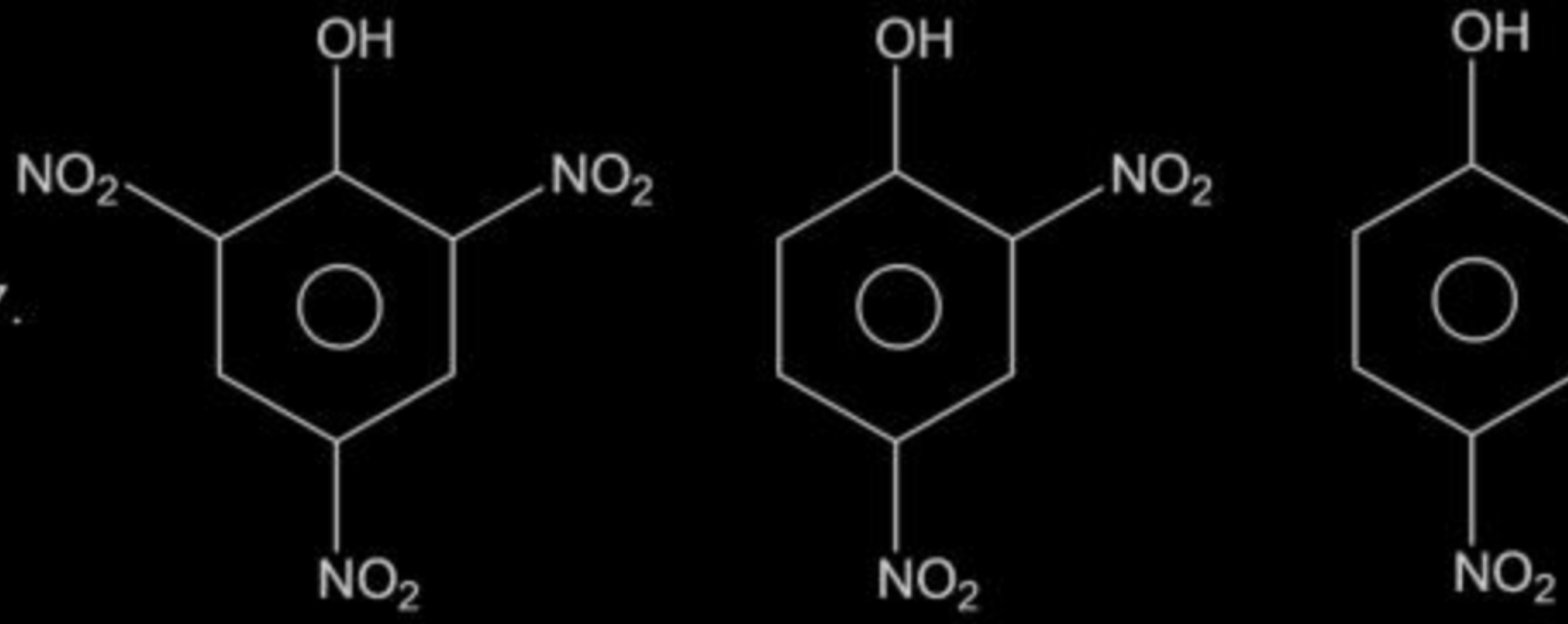
5. 

a>b>c>d>e

6. 

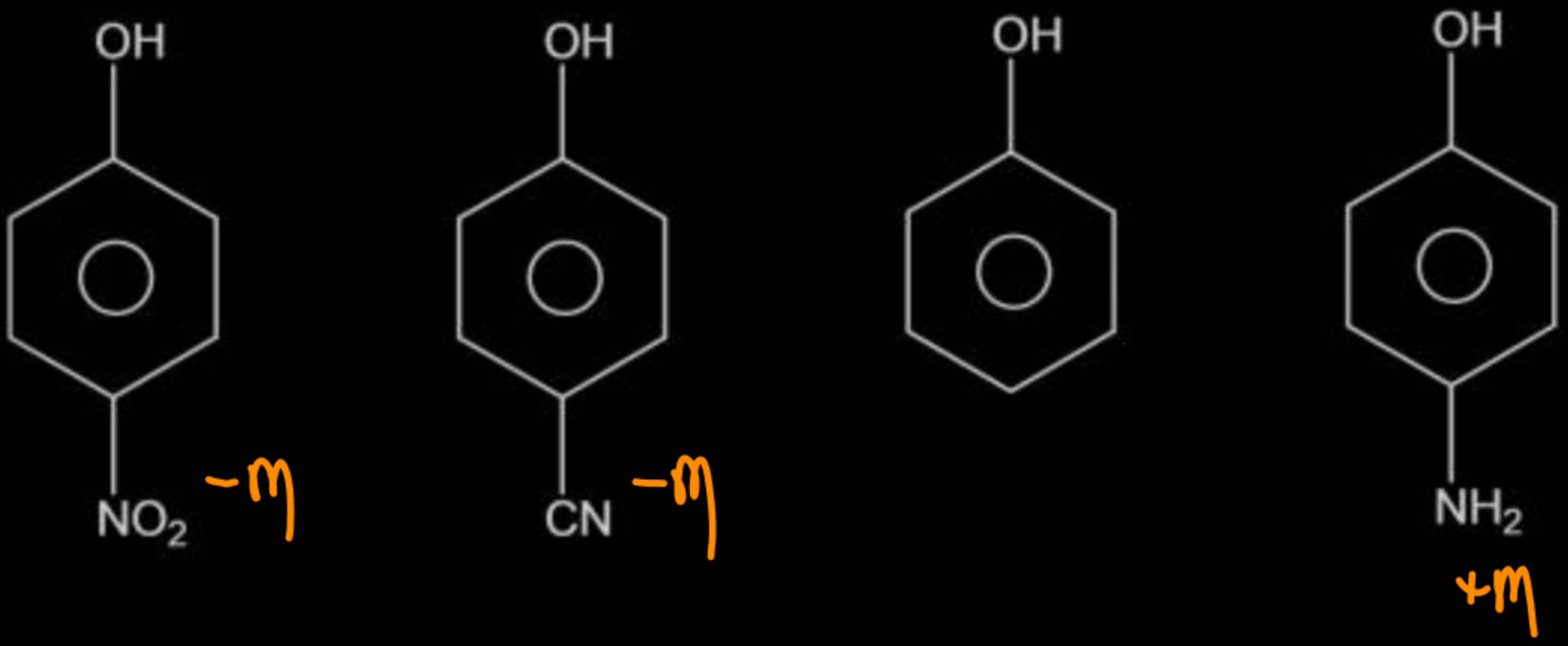
c>b>a>d

7.

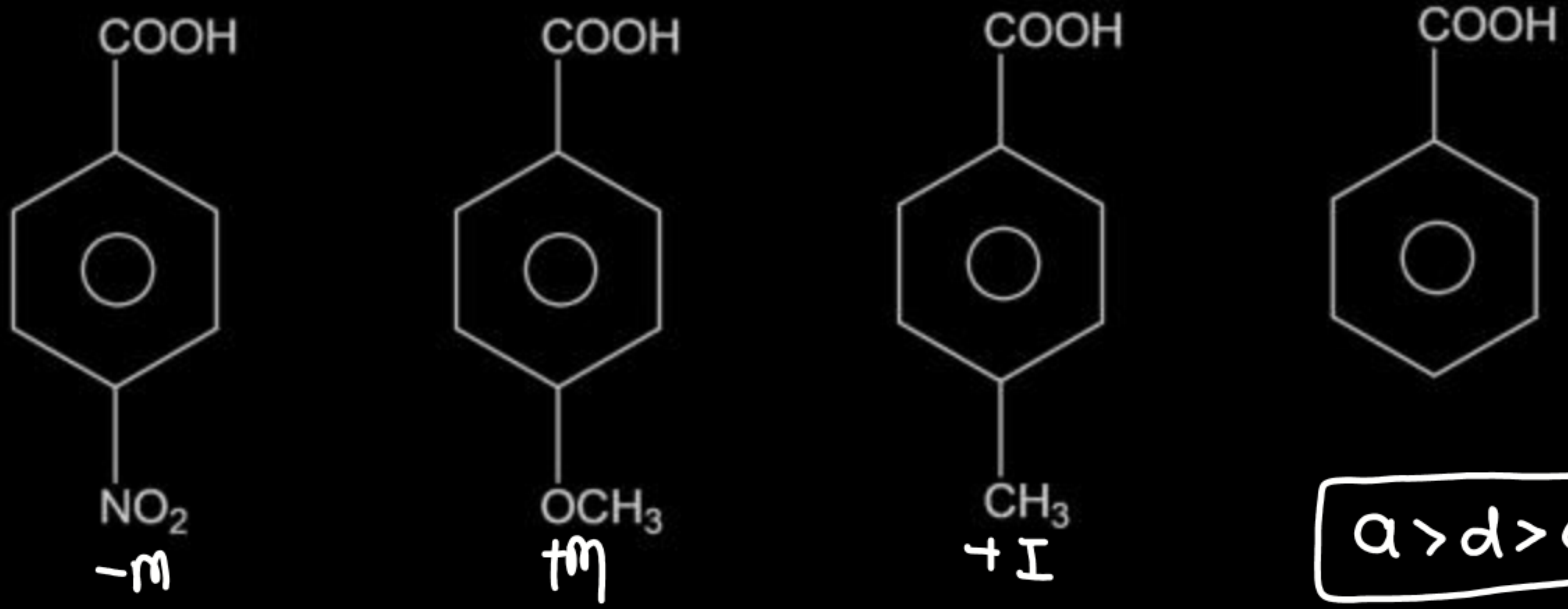


a>b>c

8.

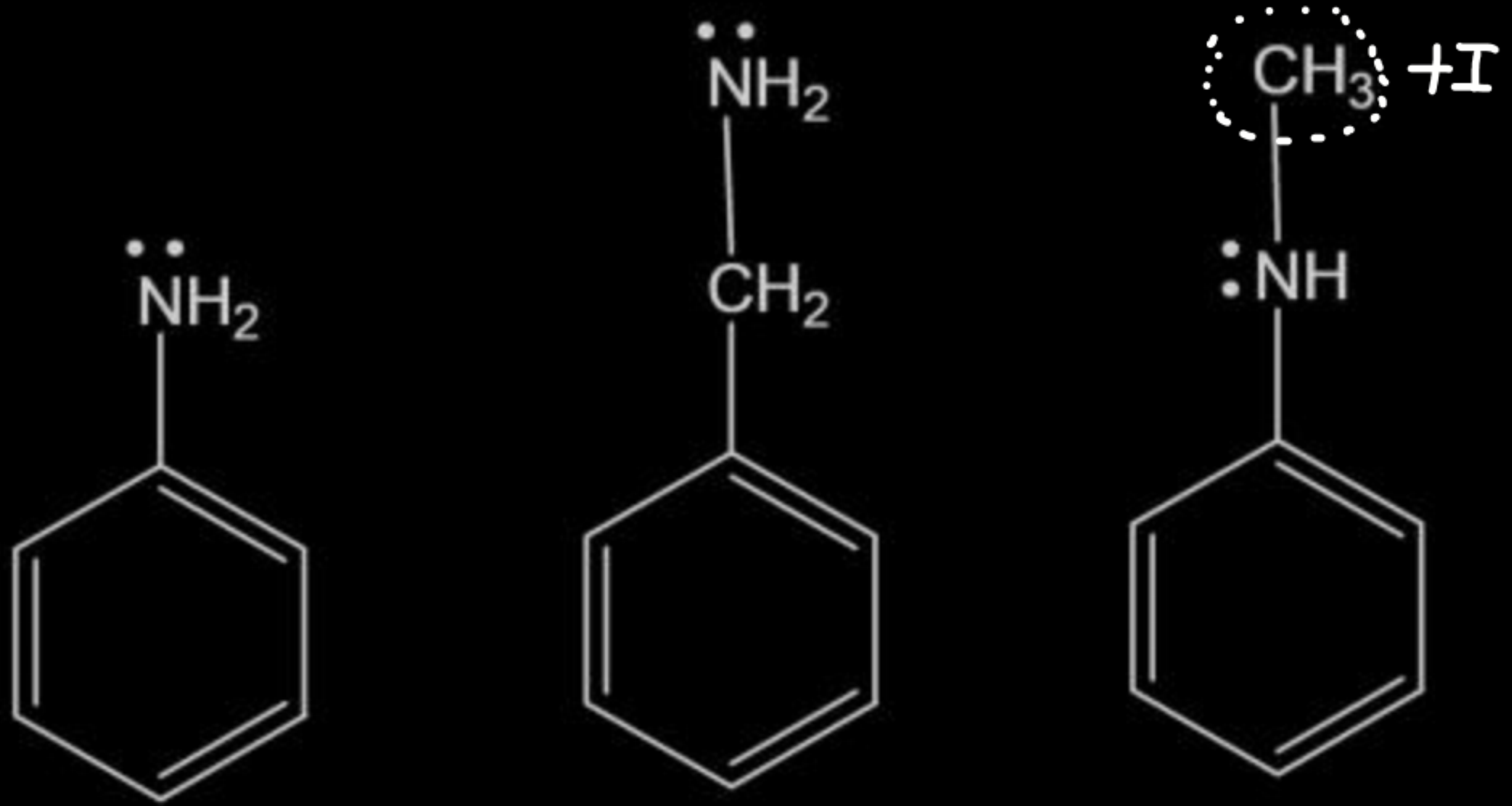


a>b>c>d

9. 

a > d > c > d

*** Basic Strength: ($\propto +m \propto \frac{1}{-m}$)**

1. 

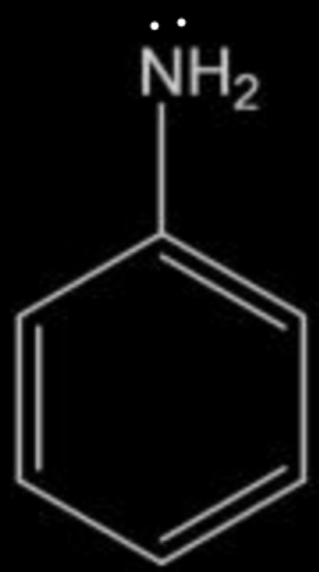
lp→Reso
कम donate

lp Reso ✗
loyal lp
ज्यादा donate

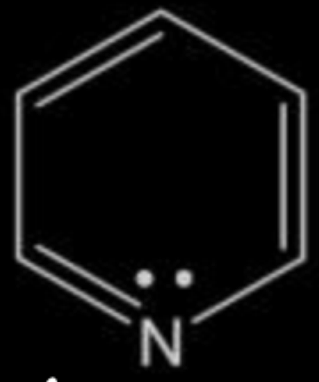
lp Reso ✓

b>c>a

2.



lp → Reso ✓



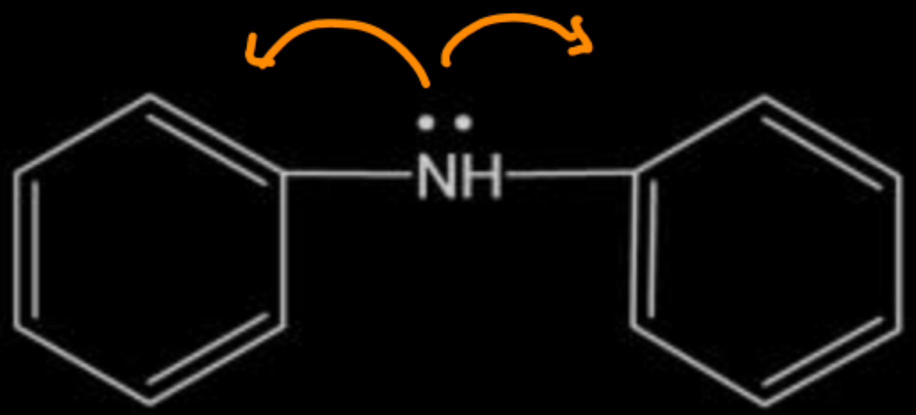
lp – Reso ✗ (more EN)

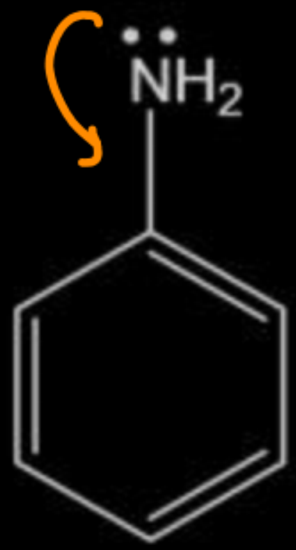


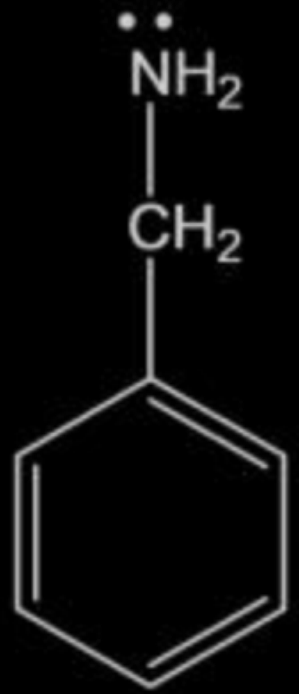
lp → Reso ✗ (less EN)

c > b > a

3.







c > b > a

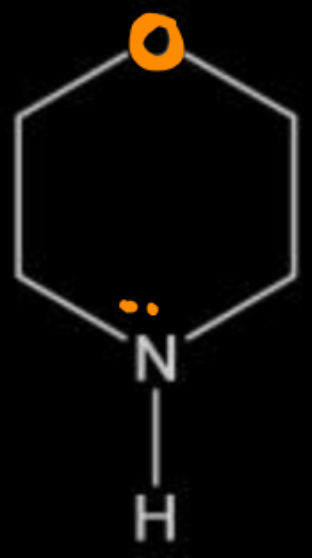
4. $CH_3-\ddot{N}H_2$ $\quad CH_2=\ddot{N}H$ $\quad C\equiv\ddot{N}$ $\quad$ a > b > c

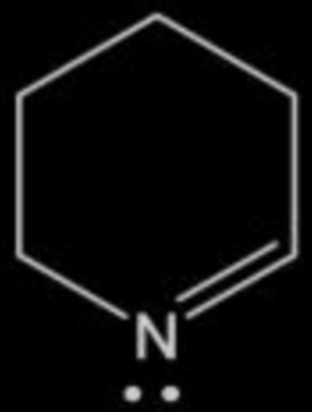
lessen (under CH_3-NH_2)
sp^3

more En (under $C\equiv N$)
sp N

5.

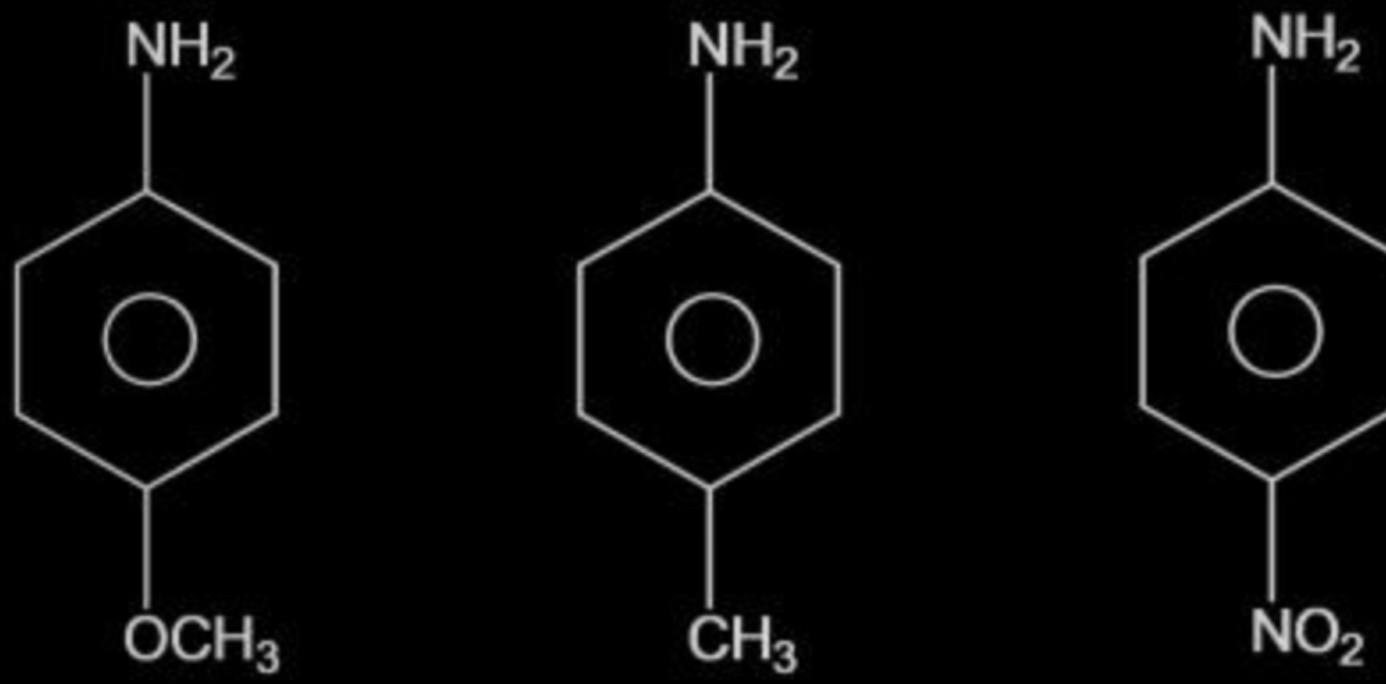






a > b > C

6.



(Q) Compare rate of reaction with $AgNO_3$







40 Que → Telegram

solve

Vtsirofficial

Resonance Effect

Mesomeric Effect



→ direction of Reso is not fixed → L to R. / → R to L.



→ direction of Reso → Fix → R to L.



→ direction of Reso → Fix → L to R.

Mesomeric effect | Resonance effect → If atom | group of atom fixes the direction of Resonance is Called R effect | M effect.

+M effect +R effect

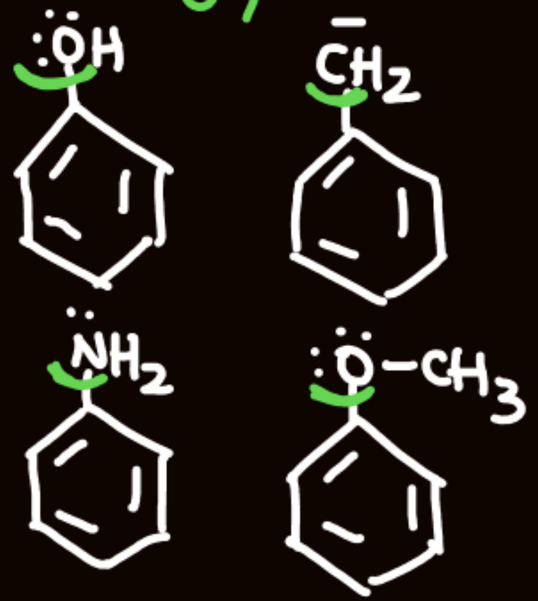
Atom/Group of atom which donates e^- through Resonance → +M/+R.

Directly attatched atom to Resonance → −ve charge/lone pair

$CH_2=CH-CH=CH-\overset{\ominus}{C}H_2$

$CH_2=CH-CH=CH-\ddot{N}H_2$

$CH_2=CH-CH=CH-\ddot{O}-H$



−M effect −R effect

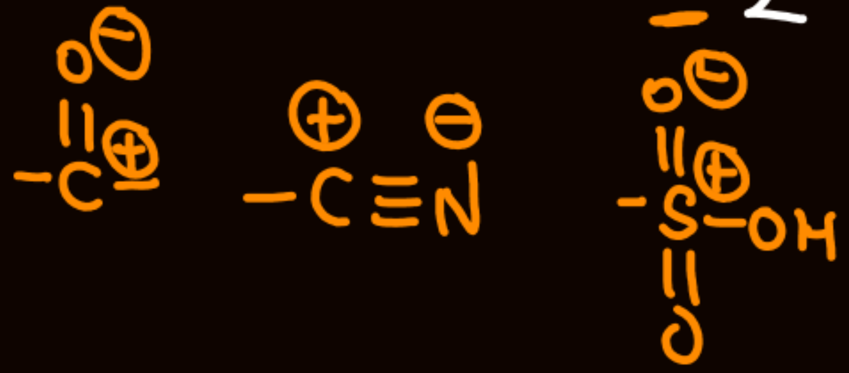
Atom/group of atom which withdraws e^- through Resonance → −M/−R.

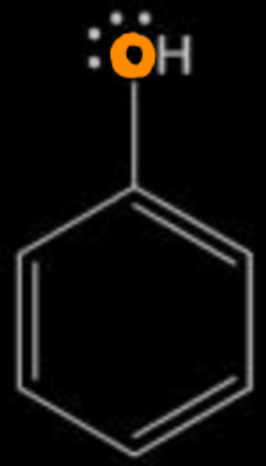
Directly attatched atom to Resonance →
1. Polar Pi Bond
2. +ve charge with Vacant orbital
3. Vacant orbital.

$CH_2=CH-CH=CH-\overset{O}{\overset{\|}{C}}-H$

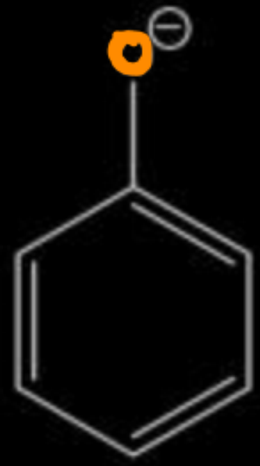
$CH_2=CH-CH=CH-\overset{\oplus}{C}H_2$

$CH_2=CH-CH=CH-BH_2$

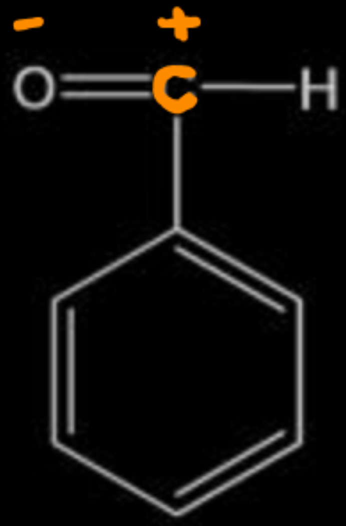




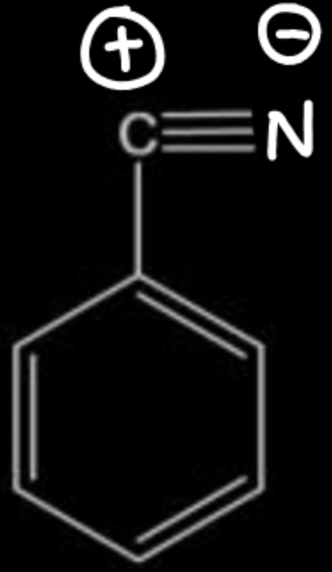
+M/+R



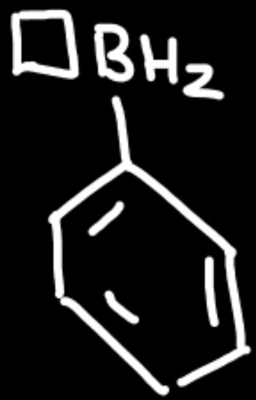
+M/+R



−M/−R



−M/−R



−M/−R



−M/−R



−M/−R

Que arrange in order of strength of +M or −M.

(+M) Q1 $-\overset{\ominus}{C}H_2$ $-\overset{\ominus}{N}H$ $-\overset{\ominus}{O}$ $-\ddot{N}H_2$ $-\overset{\ominus}{S}$

2nd Period (Unstable) | 3rd Period (Stable)

$-\overset{\ominus}{C}H_2 > -\overset{\ominus}{N}H > -\overset{\ominus}{O} > -\ddot{N}H_2 > -\overset{\ominus}{S}$

(−M) Q2 $-NO_2 > -CN > -CHO$

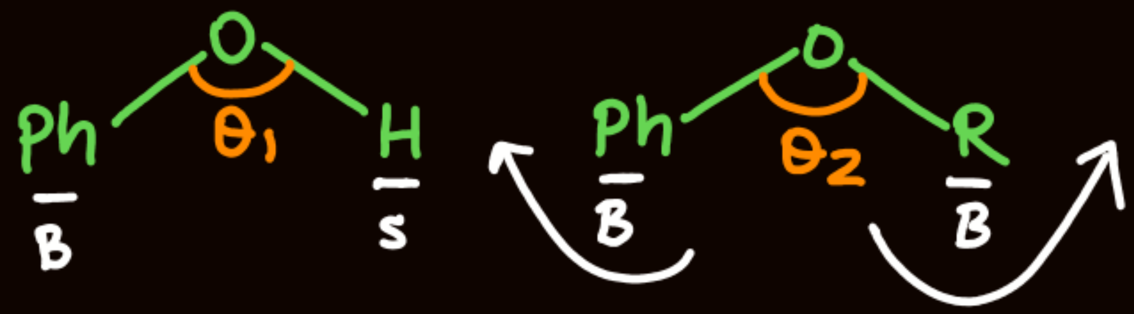
$-N(=O)\rightarrow O$ — sp^2 N (4.1)

$-C\equiv N$ — sp C (3.25)

$-\overset{O}{\overset{\|}{C}}-H$ — sp^2 C (2.75)

(+M) Q3 $-\ddot{O}H > -\ddot{O}R$

BA ∝ %S   EN ∝ %S



$\theta_1 < \theta_2$

%S ↑

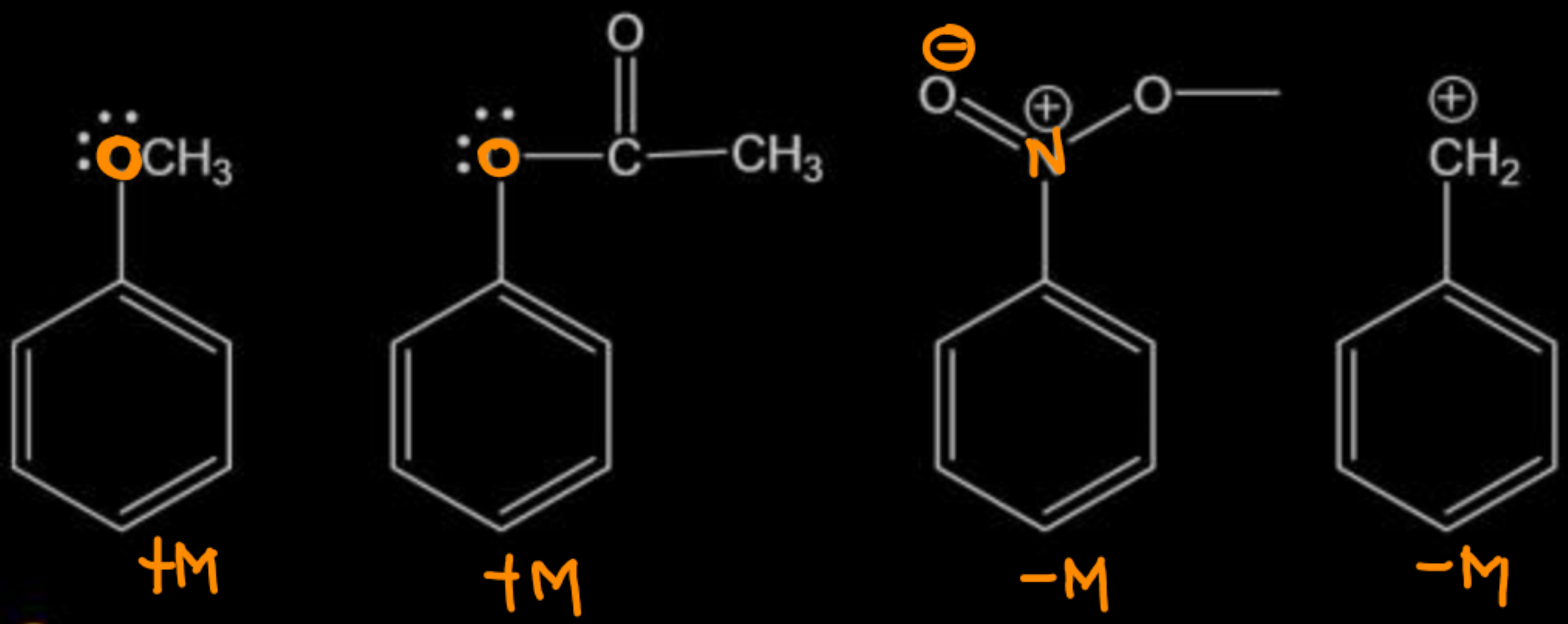
EN ↑

+M → $-O-H > -O-R$

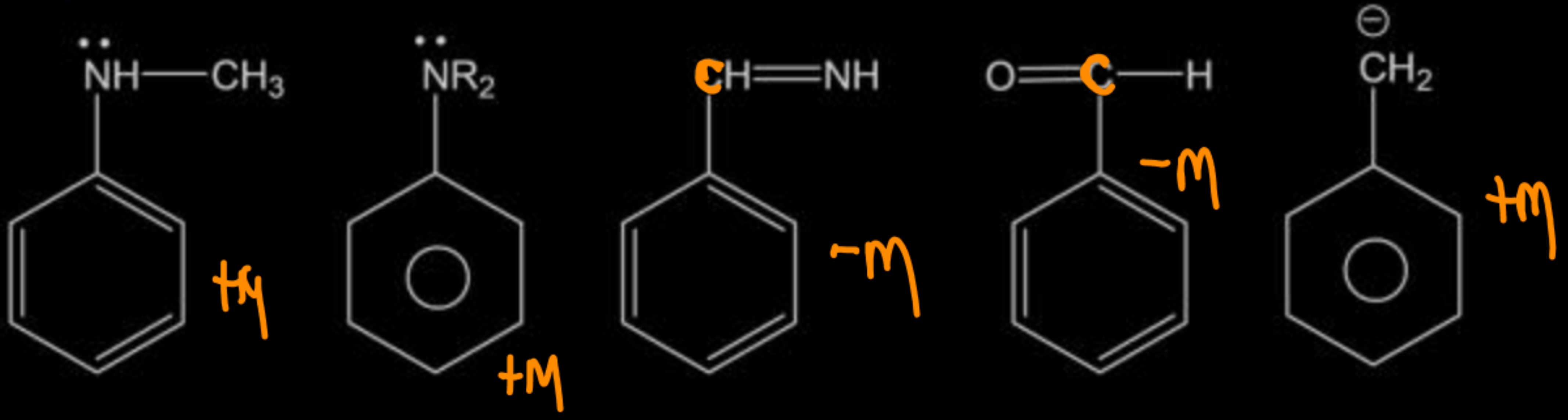
−I order	$-OR > -OH$
+M order	$-OR < -OH$

Which of the following compounds show +M or −M.

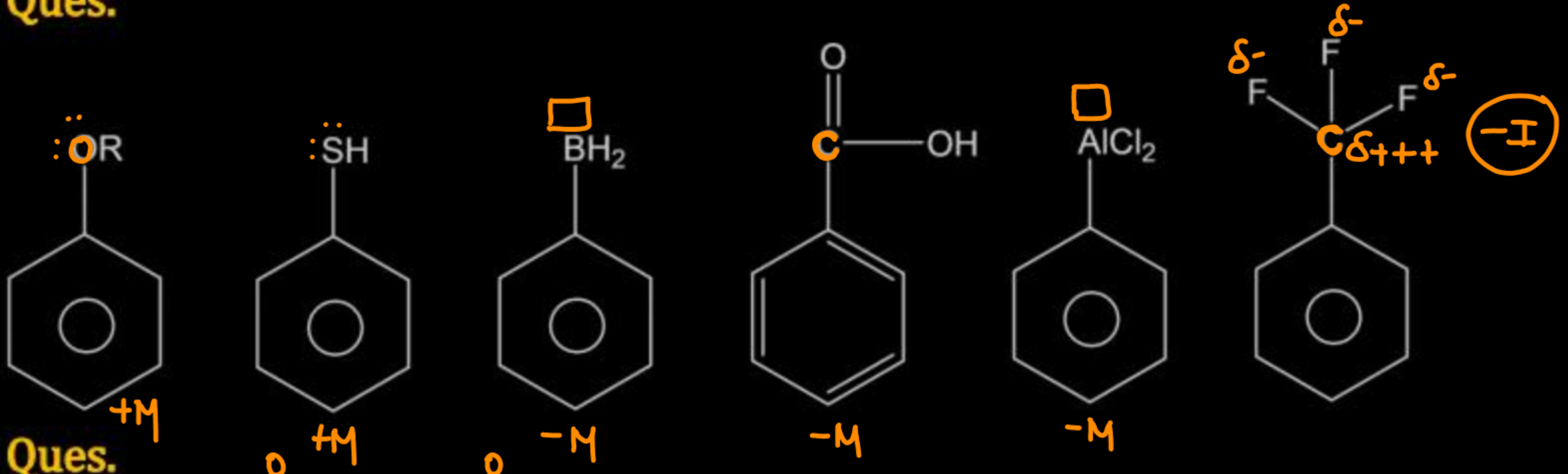
Ques.



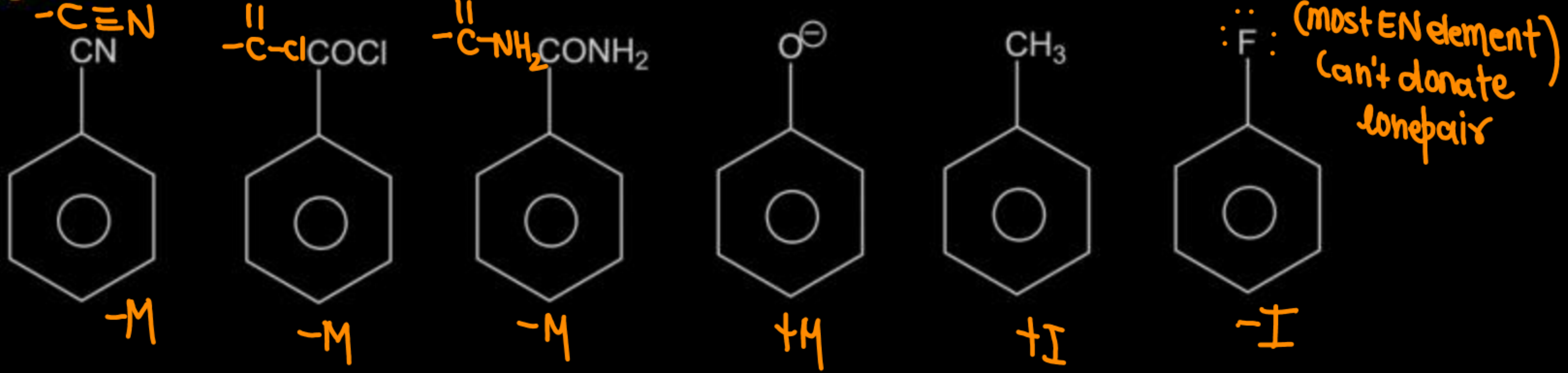
Ques.



Ques.


OR
SH
BH_2
OH
$AlCl_2$
F
δ-
δ+++
−I
+M
+M
−M
−M
−M

Ques.


−C≡N
CN
COCl
$CONH_2$
CH_3
F
(most EN element)
(can't donate lonepair
−M
−M
−M
+M
+I
−I

There are some groups which shows both +M/−M effect.

(1) $-\ddot{N}=O$ +M/−M

$CH_2=CH-\overset{+}{C}H-\ddot{N}=O$ (+M)

$CH_2=CH-\overset{\ominus}{C}H-\ddot{N}=O$ (−M)

(2) $-\ddot{N}=\overset{+}{N}H_2$ +M/−M

$CH_2=CH-\overset{+}{C}H-\ddot{N}=\overset{+}{N}H_2$ (+m)

$CH_2=CH-\underset{-}{C}H-\ddot{N}=\overset{+}{N}H_2$ (−M)

(3) $-\ddot{Cl}:$ lp → +m
vacant d orbital → −M

(4) $-\ddot{Br}:$ "

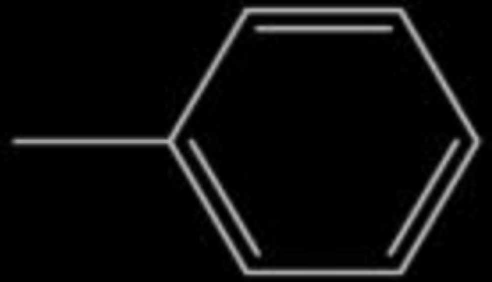
(5) $-\ddot{I}:$ "

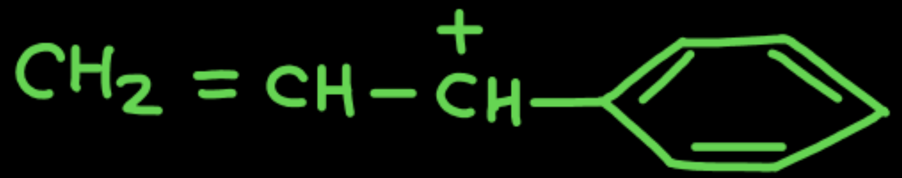
* $-\ddot{F}:$ no +M → most EN atom. Can't donate lp.
no −M → Vacant orbital absent.

(6) $-CH=CH_2$

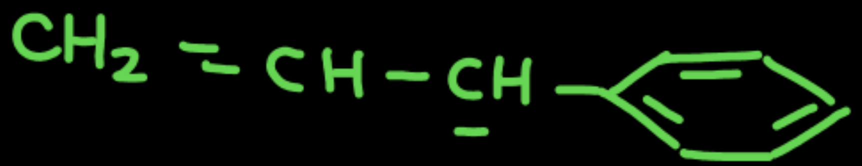
$CH_2=CH-\overset{+}{C}H-CH=CH_2$ (+M) donate → πe^- density

$CH_2=CH-\overset{-}{C}H-CH=CH_2$ (−M) accept → Reso ✓

(7) 



+M

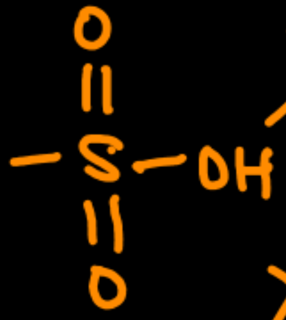


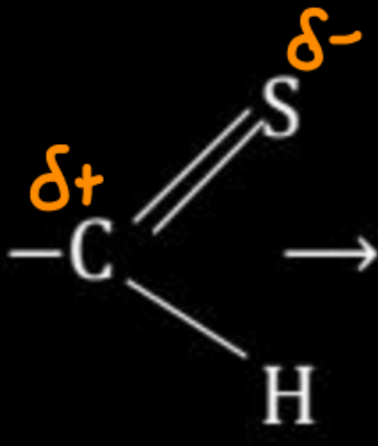
−M

sp & sp^2C → more En
sp^3C → less En

Group	Structure	+I effect	−I effect	+M effect	−M effect
$-NO_2$	$-N(=O)\rightarrow O$	✗	✓	✗	✓
$-CH_3$	$-CH_3$ (C bonded to three H)	✓	✗	✗	✗
$-CF_3$	$-CF_3$ (C bonded to three F), $\delta+++$	✗	✓	✗	✗
$-NO$	$-\ddot{N}=O$	✗	✓	✓	✓
$-Cl$	$-\ddot{Cl}:$	✗	✓	✓	✓
$-CHO$	$-C(=O)-H$ (sp^2C)	✗	✓	✗	✓
$-COOH$	$-C(=O)-OH$	✗	✓	✗	✓
$-COCH_3$	$-C(=O)-CH_3$	✗	✓	✗	✓
$-CONH_2$	$-C(=O)-NH_2$	✗	✓	✗	✓
$-COCl$	$-C(=O)-Cl$	✗	✓	✗	✓
$-CN$	$-C\equiv N$	✗	✓	✗	✓

	+I	−I	+M	−M
$-CH=NH \longrightarrow$	✗	✓	✗	✓
$-CH_2NH_2 \longrightarrow$	✓	✗	✗	✗
$-\ddot{N}H_2 \longrightarrow$	✗	✓	✓	✗
$-\ddot{N}H-CH_3 \longrightarrow$	✗	✓	✓	✗
$-\ddot{N}F_2 \longrightarrow$	✗	✓	✓	✗
$-SO_3H \longrightarrow$	✗	✓	✗	✓
$-\overset{+}{N}F_3 \longrightarrow$	✗	✓	✗	✗
$-\overset{O}{\overset{\Vert}{C}}-NH_2 \longrightarrow$	✗	✓	✗	✓



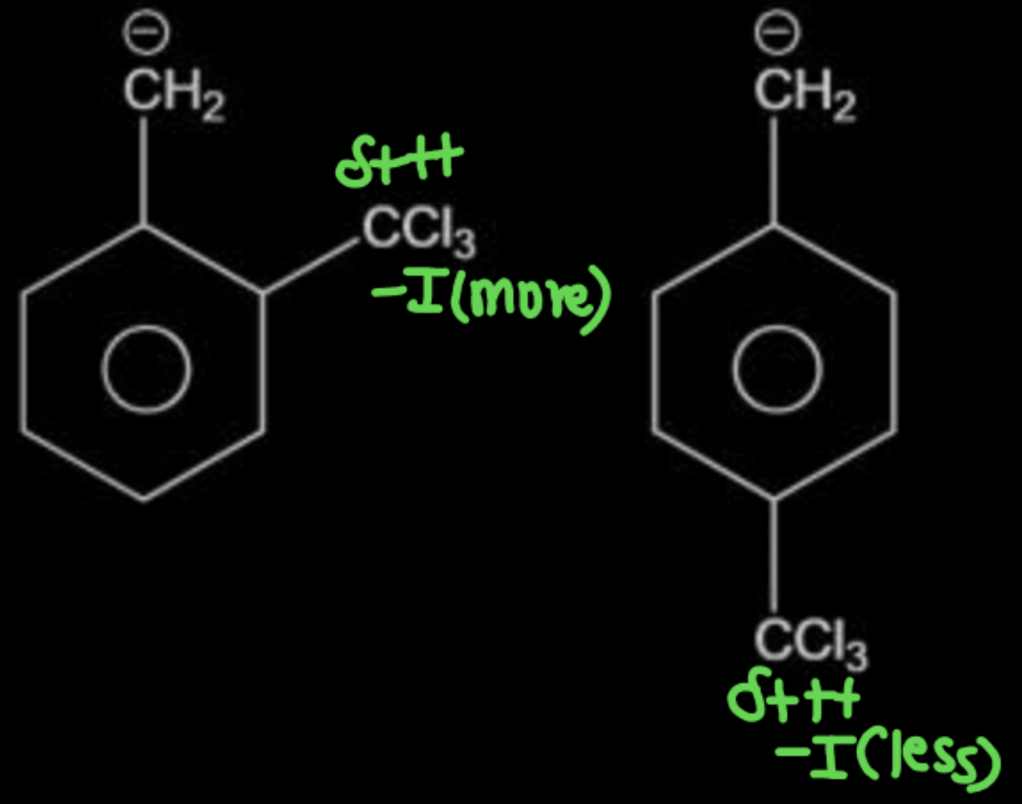
	+I	−I	+M	−M
$-N \equiv C \rightarrow$	×	✓	×	✓
$-\overset{+}{N}R_3 \rightarrow$	×	✓	×	×
$-Ph \rightarrow$	×	✓	✓	✓
 $\rightarrow$	×	✓	×	✓

$C_{EN} = 2.55$

$S_{EN} = 2.58$

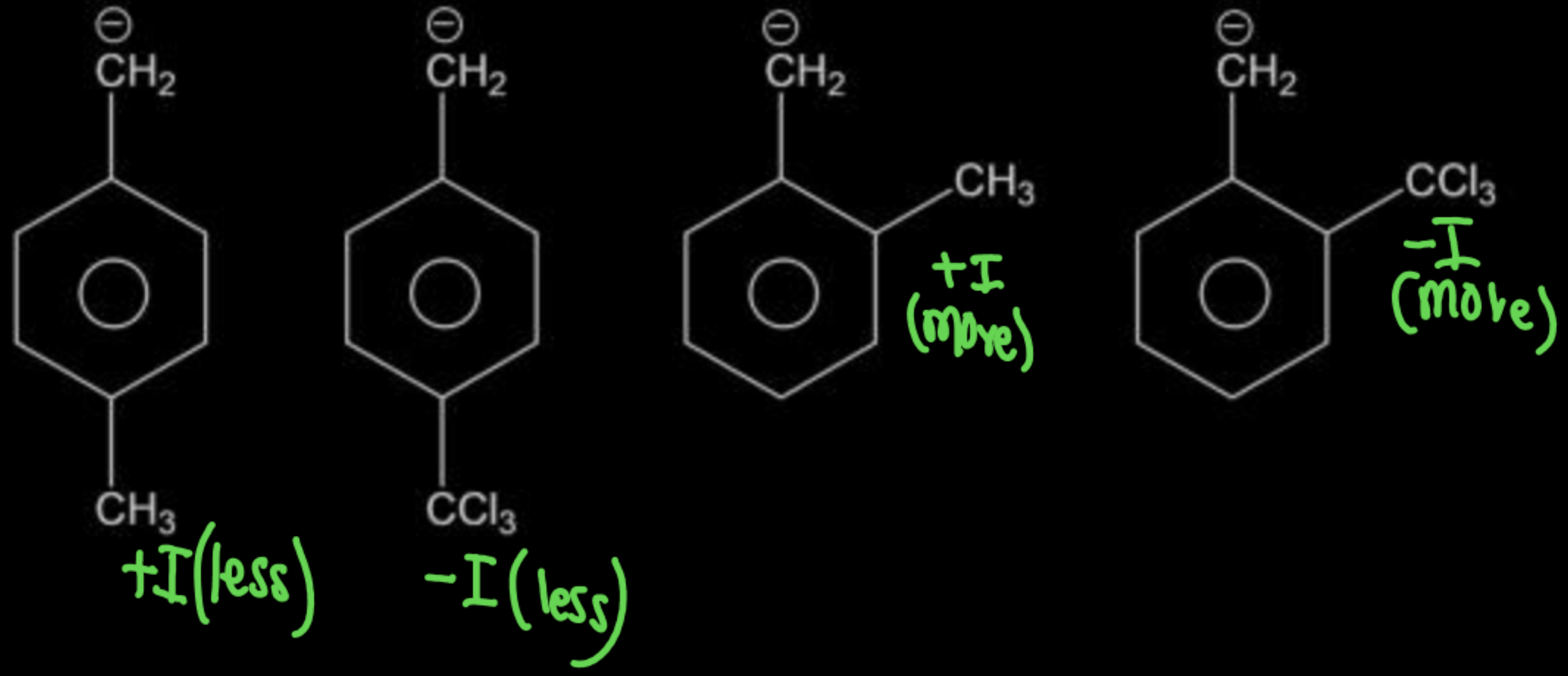
Que Compare the stability of intermediate –

Carbocation → M H I
Carbanion → M I

1. 

1 > 2

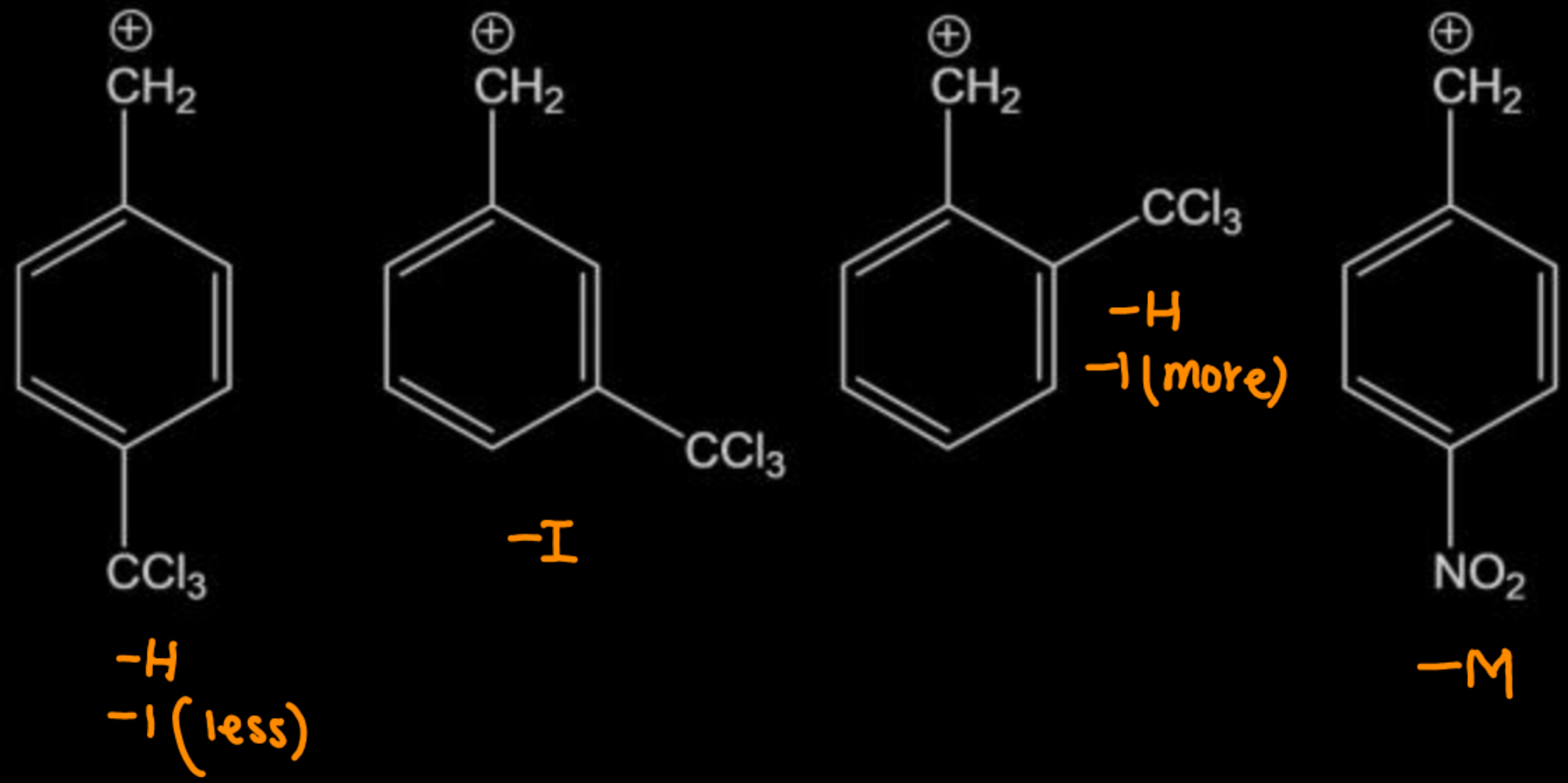
Pro

2. 

b ≈ d > a & c

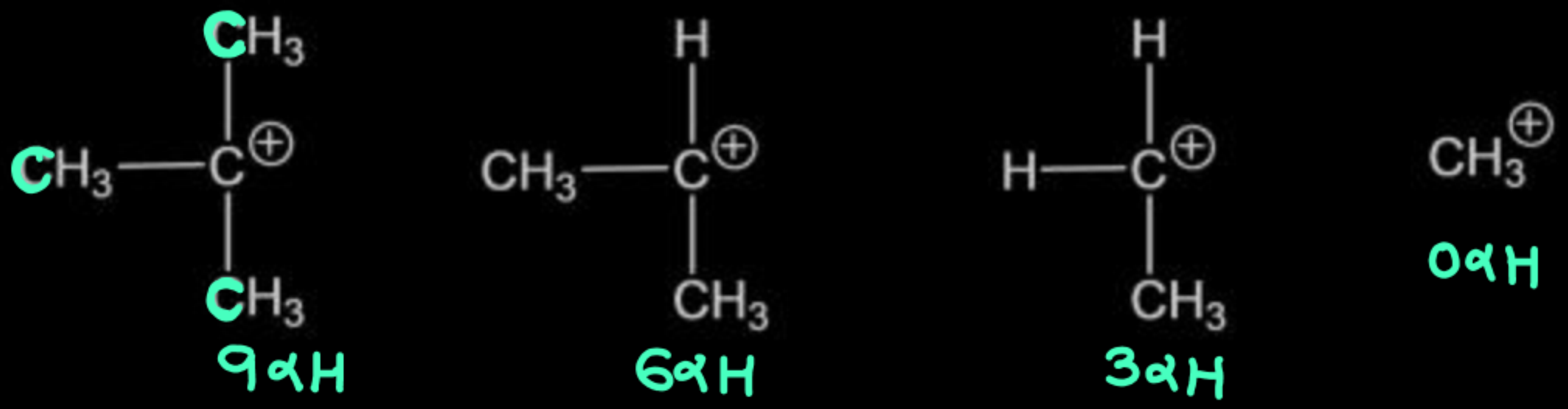
d > b > a > c

3.

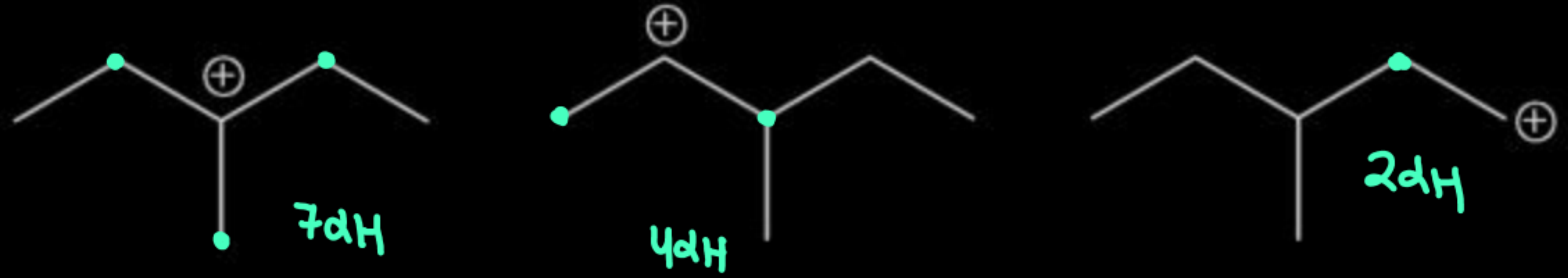


b > a > c > d

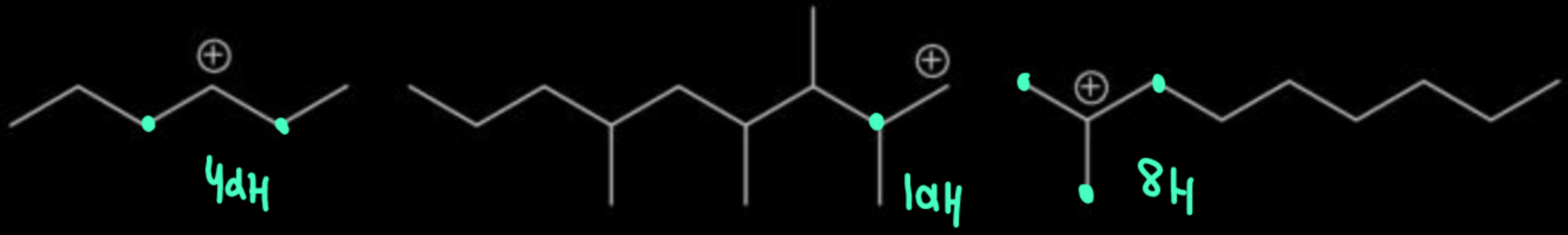
(1) Stability of carbocation: - α number of α − H

1. 

a>b>c>d

2. 

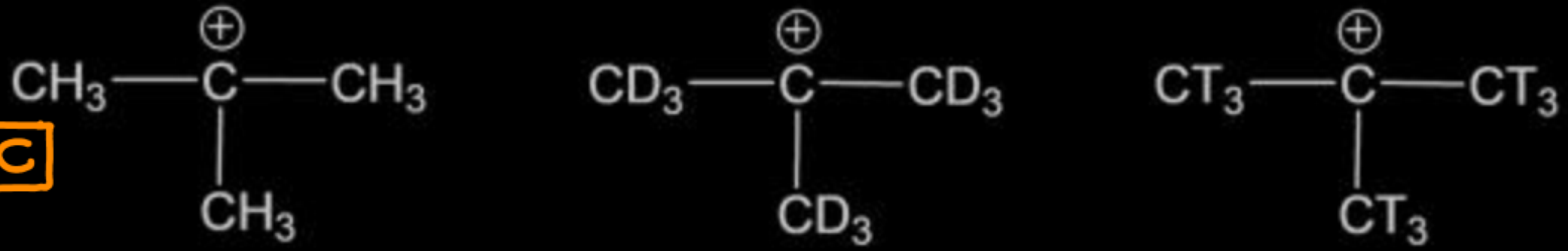
a>b>c

3. 

c>a>b

9αH 9αD 9αT

4.



a > b > c

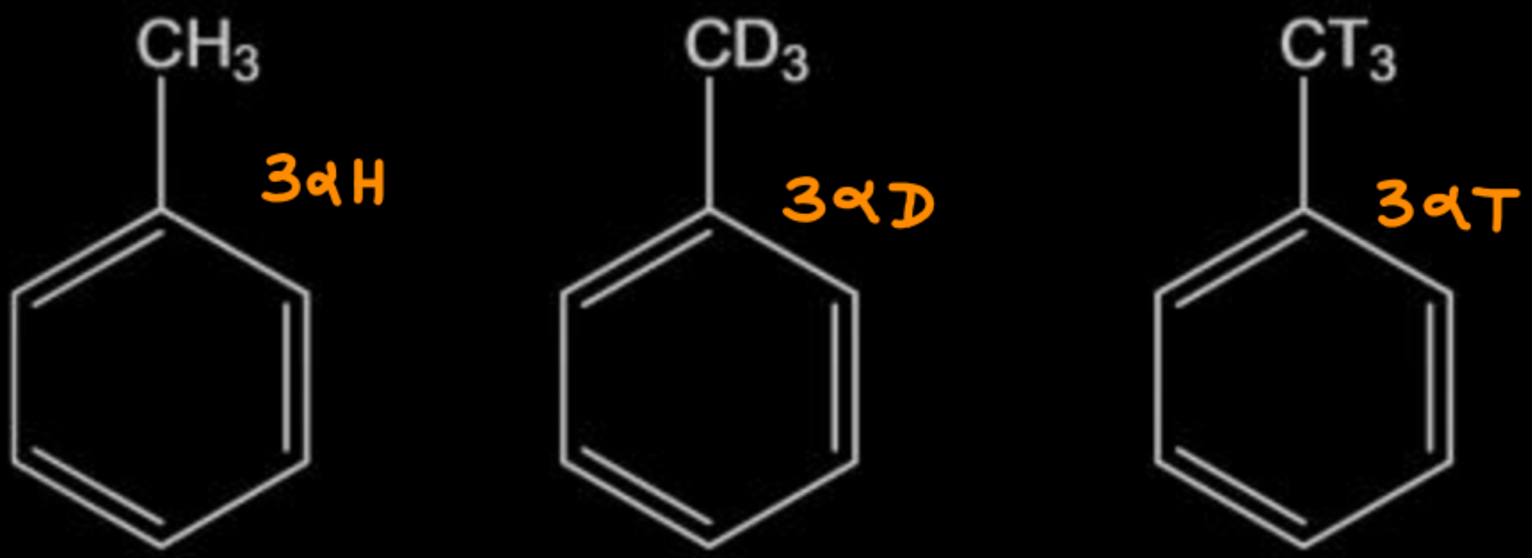
note

+I order ⇒ T > D > H

Hc order ⇒ H > D > T

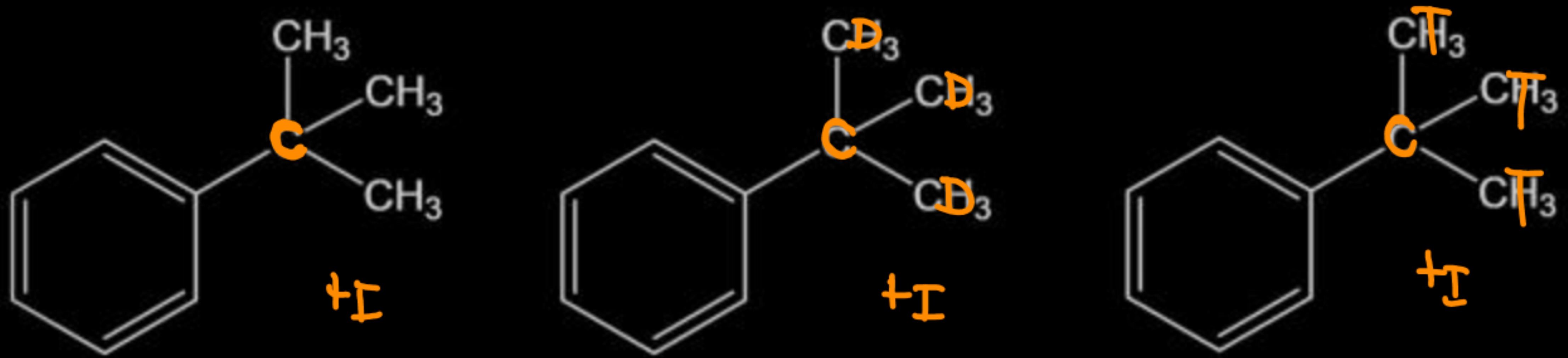
H — Hydrogen
D — Deuterium
T - Tritium
} isotopes of Hydrogen

5.



a > b > c

6.



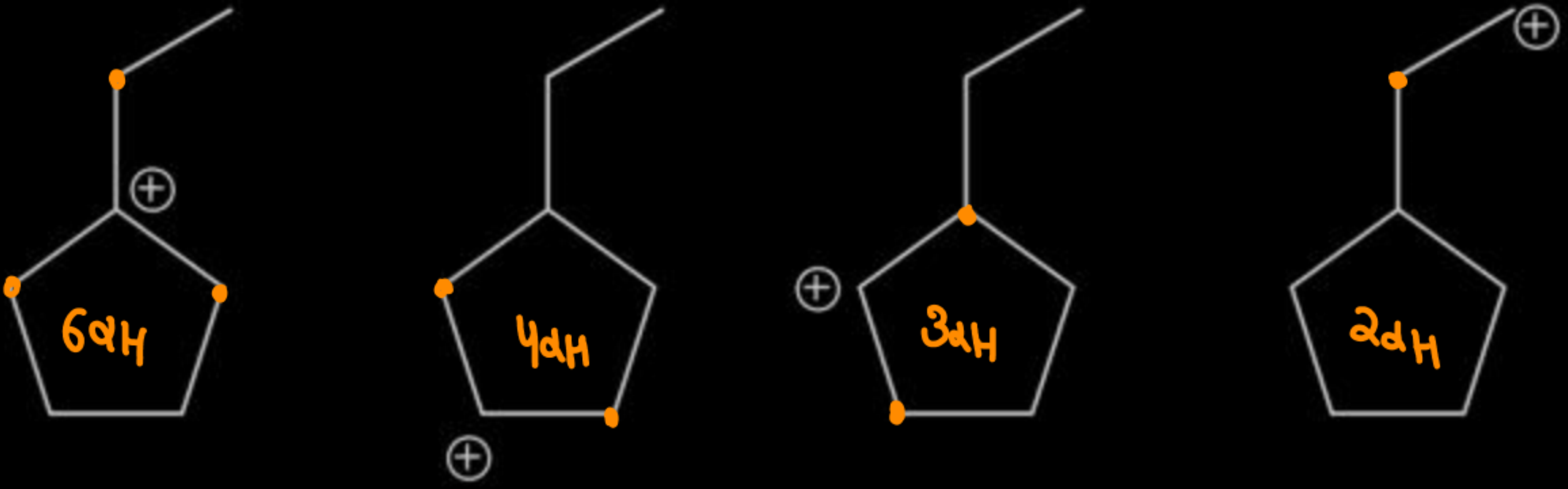
c > b > a

7. 

a>b

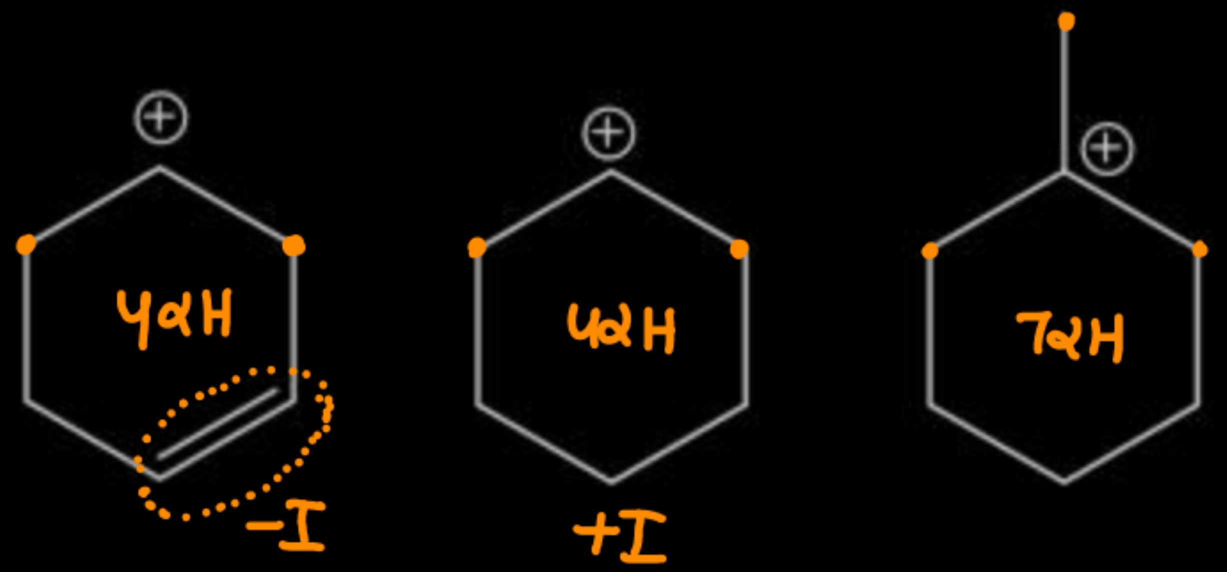
8. 

b>a

9. 

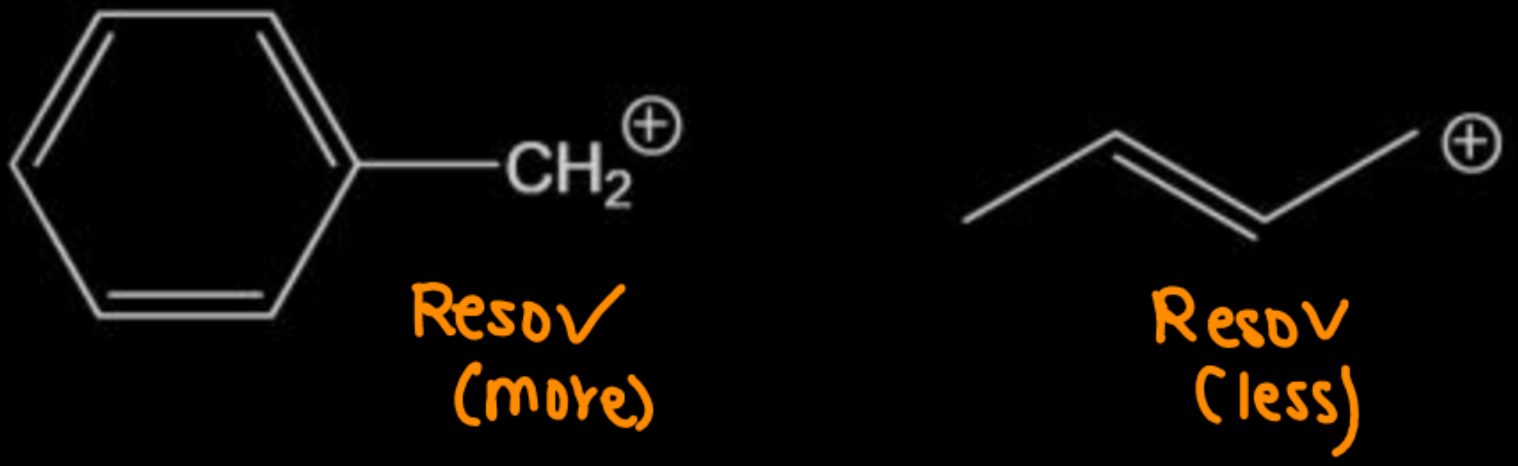
a>b>c>d

10.



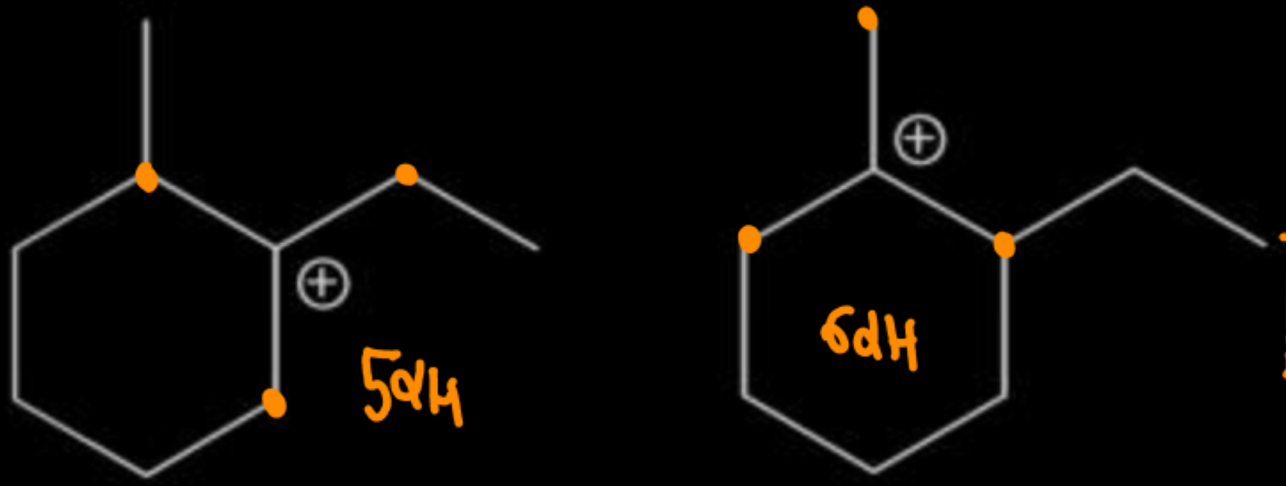
c > b > a

11.



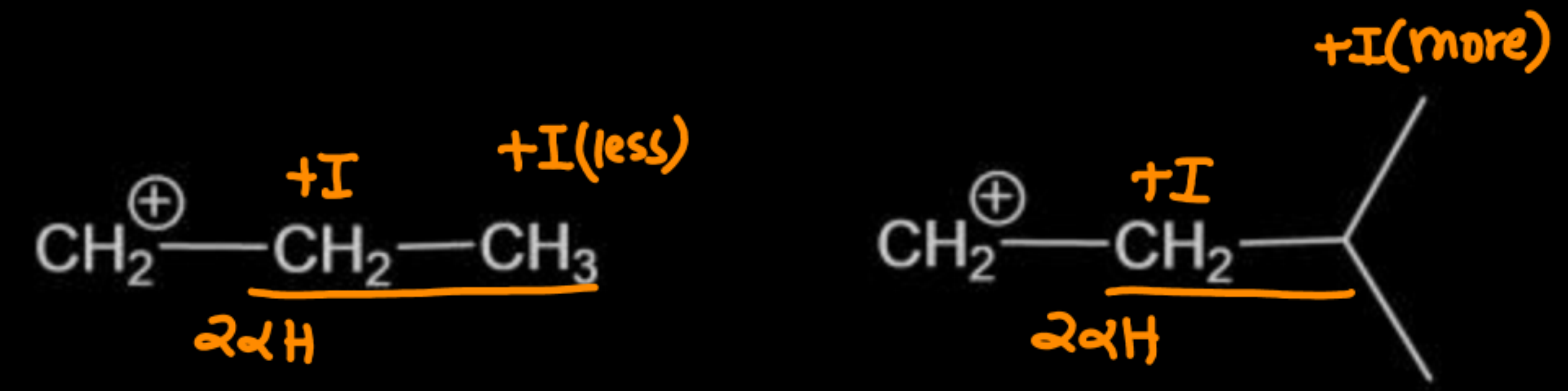
a>b

12.



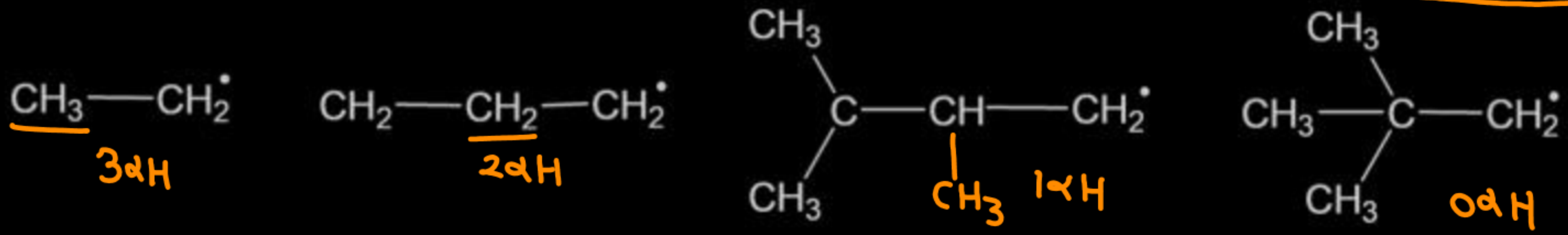
b>a

13.



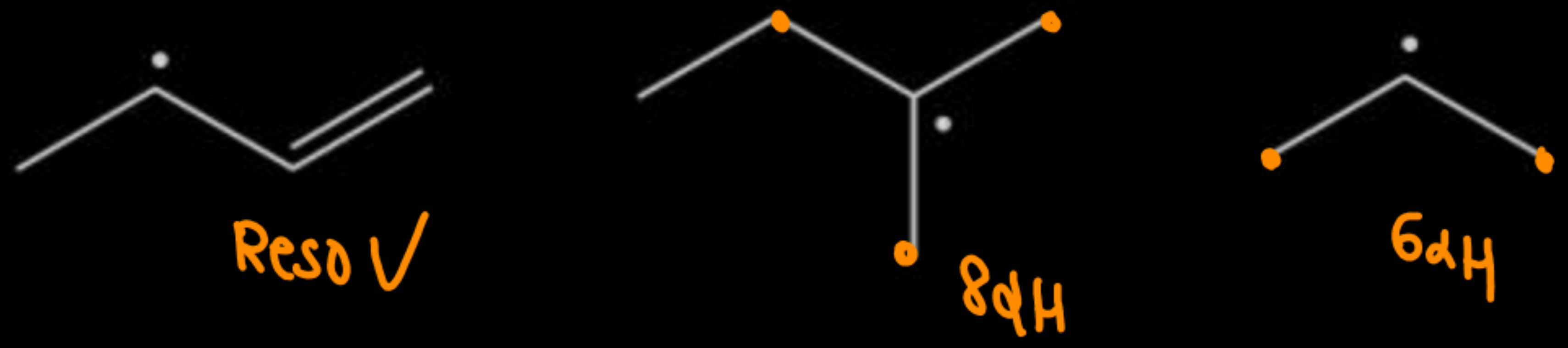
b>a

14.



a>b>c>d

15.



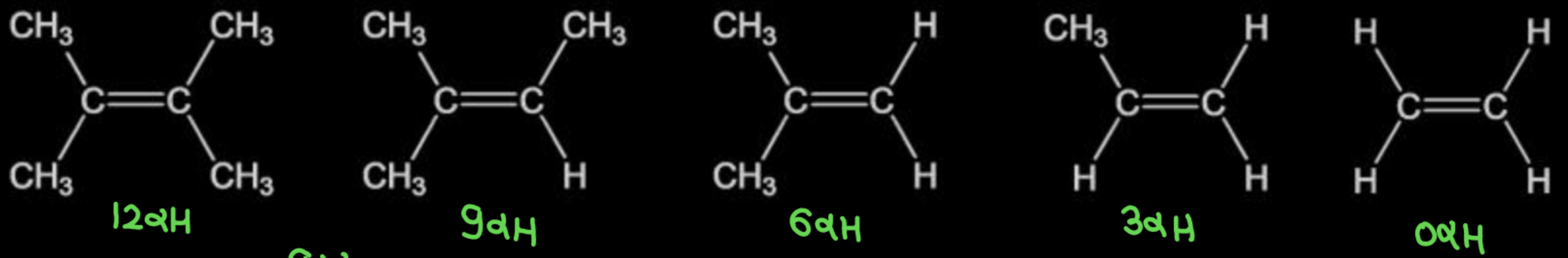
a>b>c

a > b > c > d > e > f > g > h

16. $(Ph)_3-\dot{C}H_2$ $(Ph)_2-\dot{C}H_2$ $(Ph)-\dot{C}H_2$ $CH_2=CH-\dot{C}H_2$ $CH_3-\dot{C}(CH_3)-CH_3$

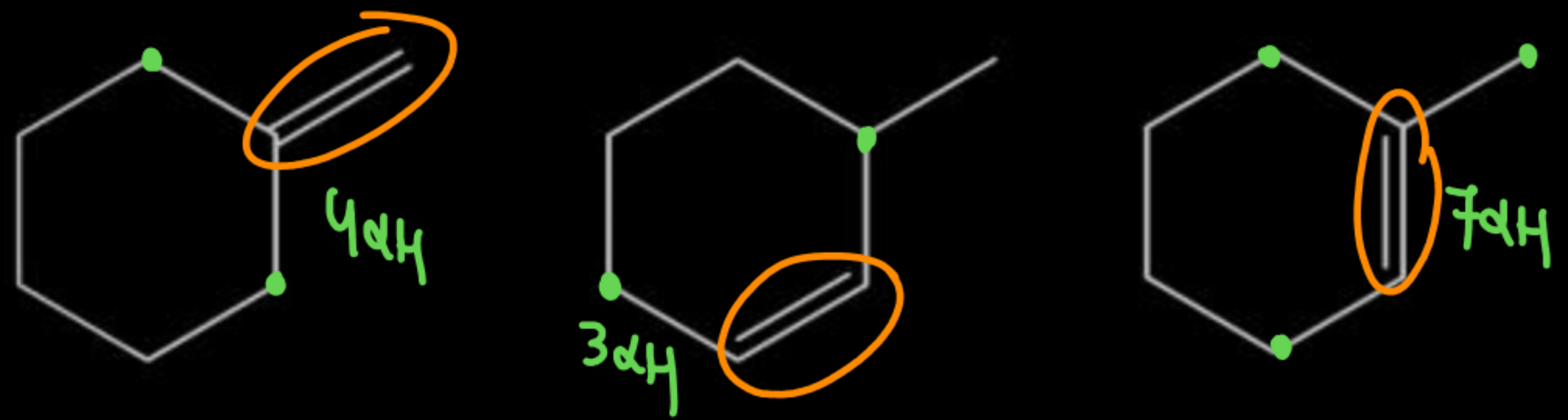
$CH_3-\dot{C}H-CH_3$ $CH_3-\dot{C}H_2$ $\dot{C}H_3$

17.



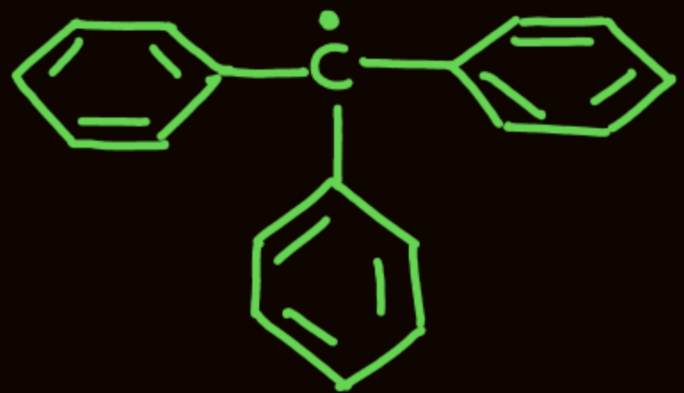
a > b > c > d > e

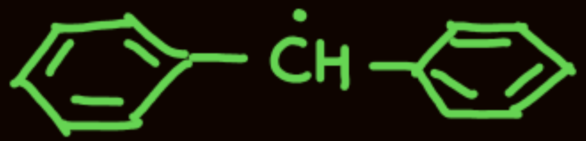
18.

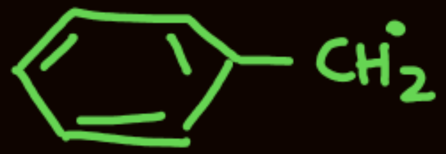


c > a > b

(16) $(Ph)_3-\dot{C}$ $\quad$ $(Ph)_2-\dot{C}H$ $\quad$ $(Ph)-\dot{C}H_2$



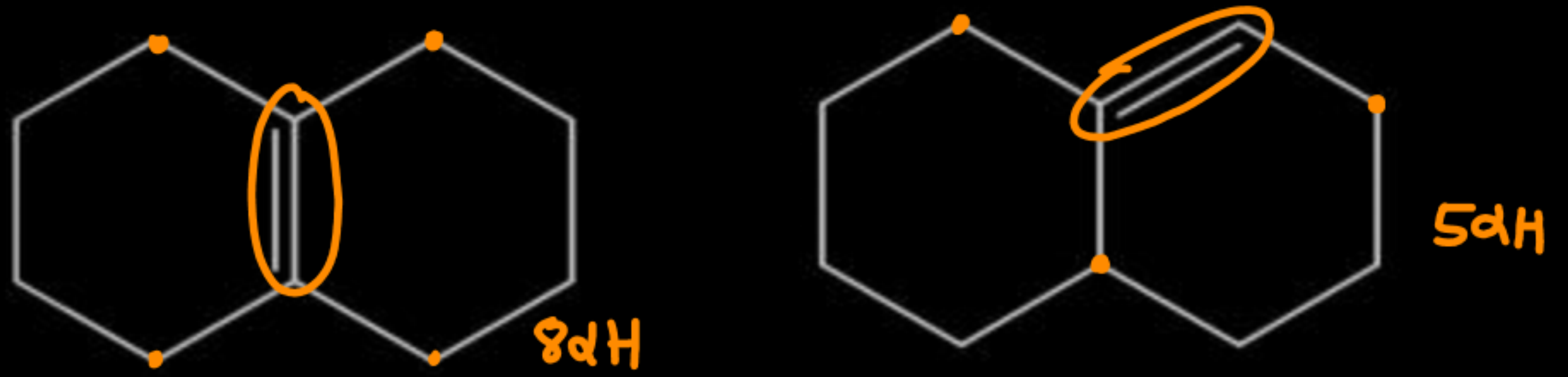




more Reso $\quad$ less $\quad$ least Reso

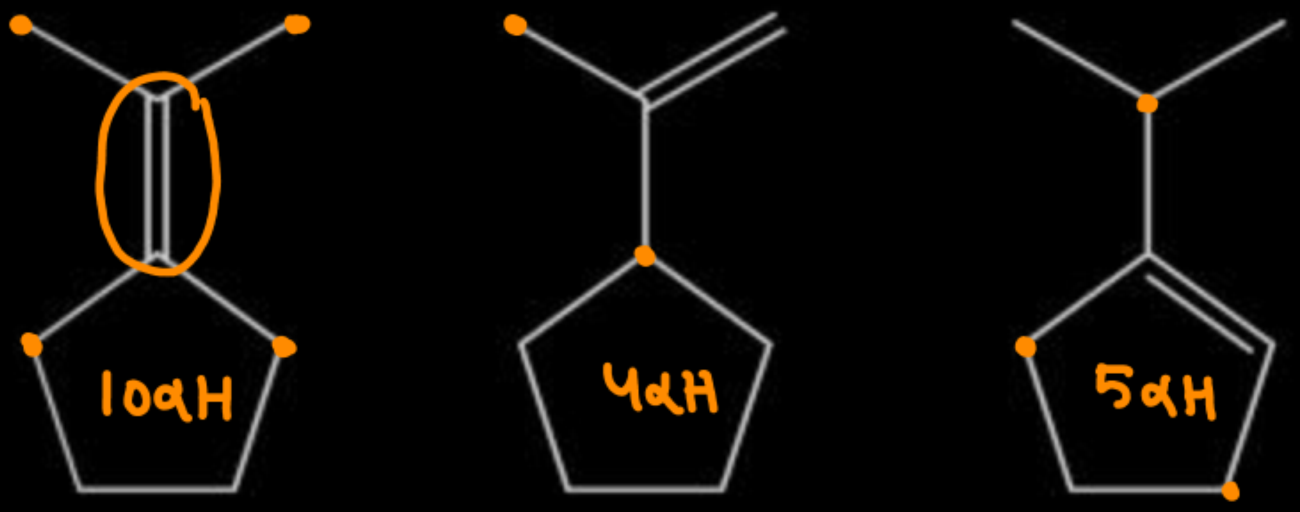
a>b>c

19.



a>b

20.



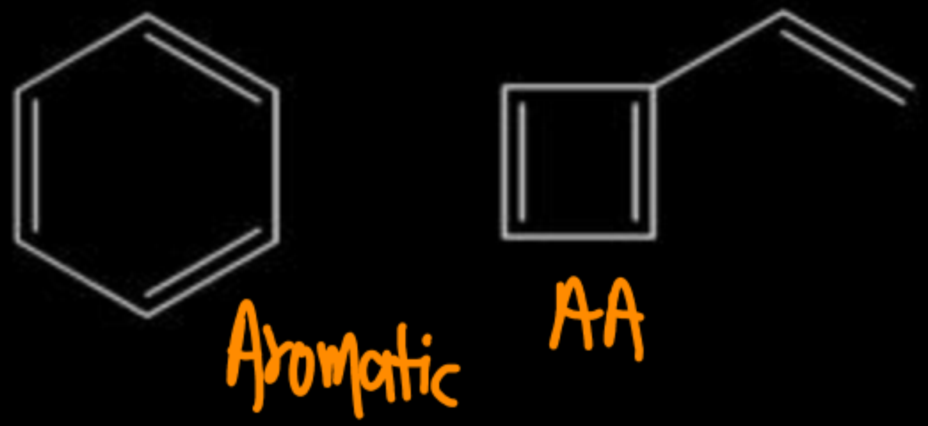
a>c>b

21.



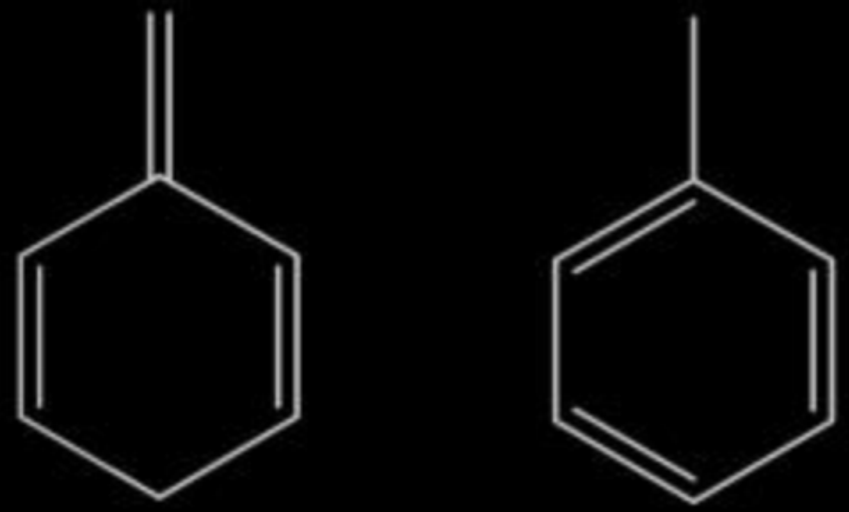
a>b

22.



a>b

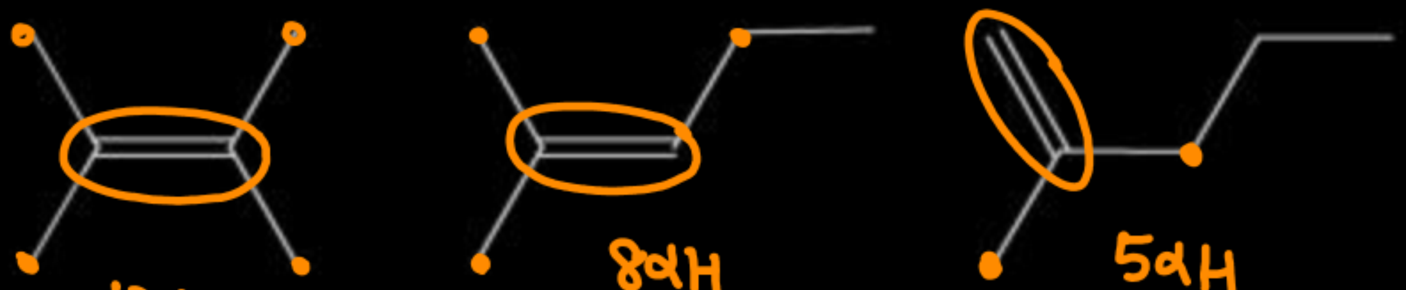
23.



NonAromatic — Aromatic

b > a

24.



12αH — 8αH — 5αH

a > b > c

25.



6αH — cis alkene

6αH — Trans alkene

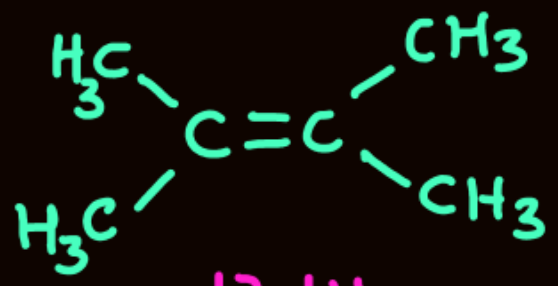
6αH — ISO alkene

alkene → I > T > C

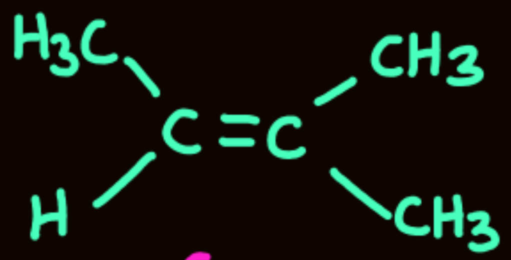
याद

चाय

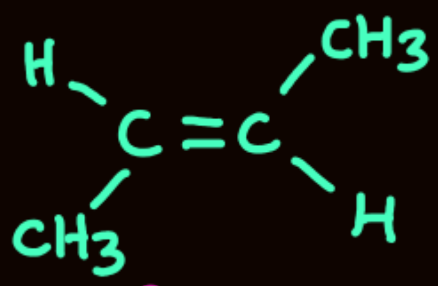
(26)



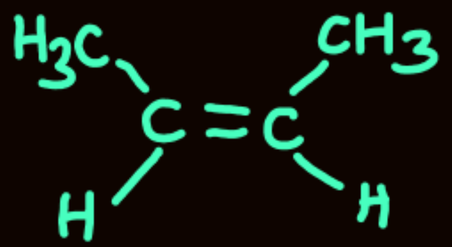
12αH



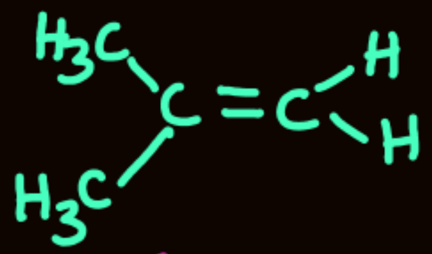
9αH



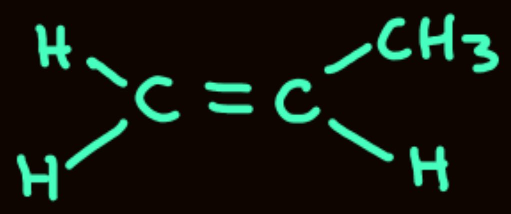
6αH



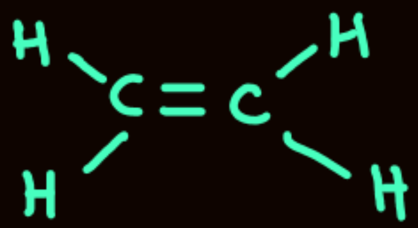
6αH



6αH



3αH



0αH

a > b > e > c > d > f > g

(e > c > d): I > T > C

Heat of Hydrogenation

→ addition of Hydrogen

Heat Energy released when Hydrogen is added to Unsaturated comp to make it Saturated, is called HOH.

Catalytic Hydrogenation

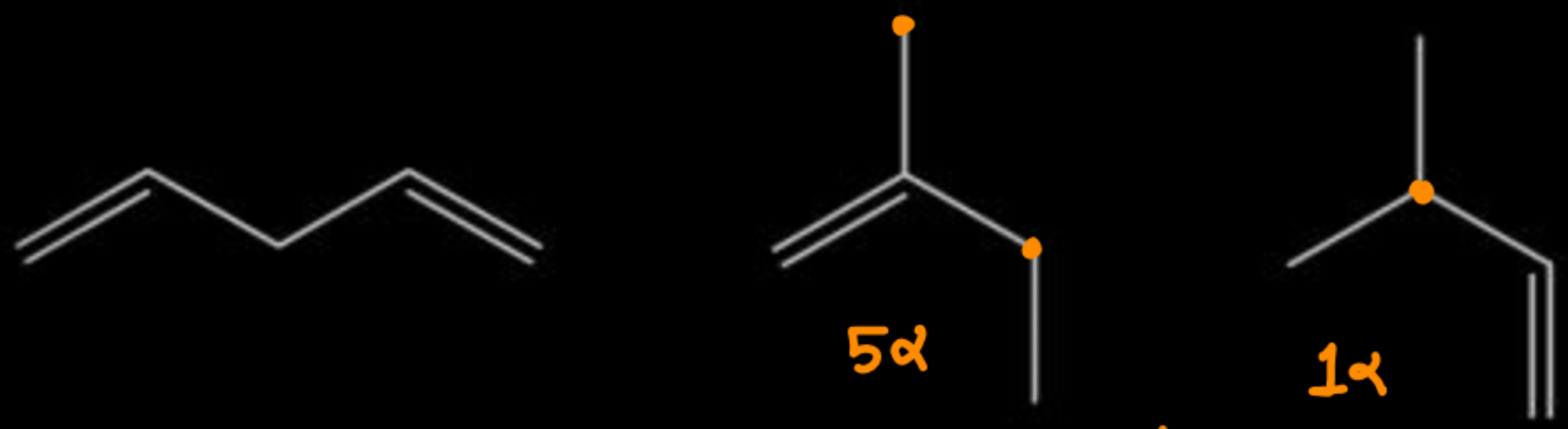
$$CH_3-CH=CH_2 \xrightarrow[Ni/Pd/Pt]{H_2} CH_3-\underset{H}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}$$

Unsaturated Comp	Saturated comp	Energy released (Heat of Hydrogenation)
(unstable)	(stable)	Exothermic
weak bond	(Strong bond)	$\Delta H = -ve$
		$\Delta H < 0$

① HOH ∝ no of π bond

if π bond is same → ② $HOH \propto \frac{1}{\text{stability}}$

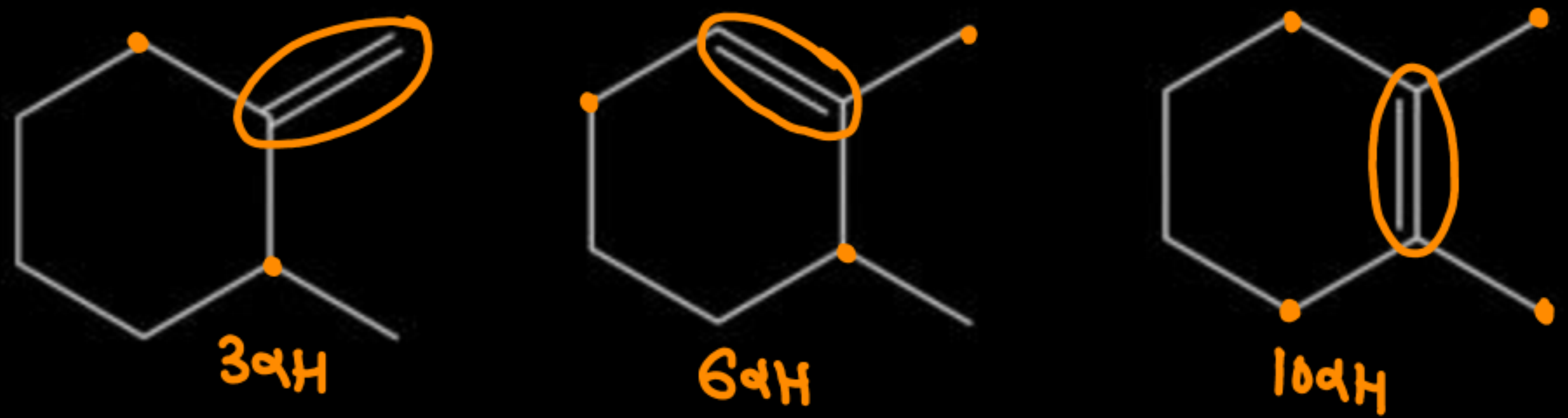
1.



Stab → b > c

HOH → a > c > b

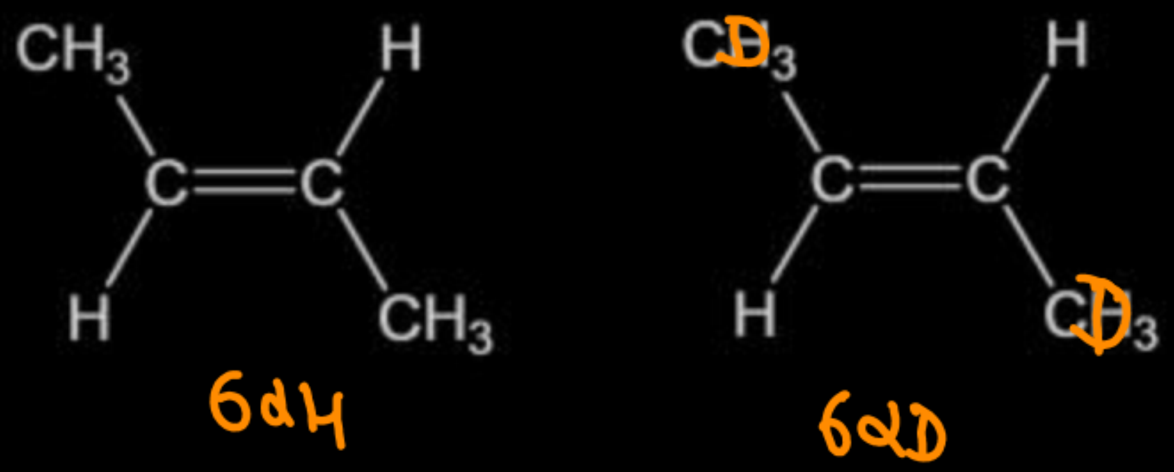
2.



Stab → c > b > a

HOH → a > b > c

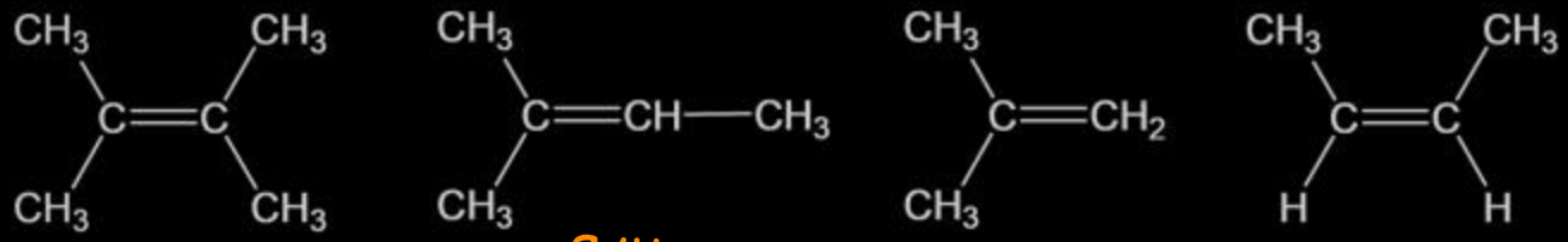
3.



Stab → a > b

HOH → b > a

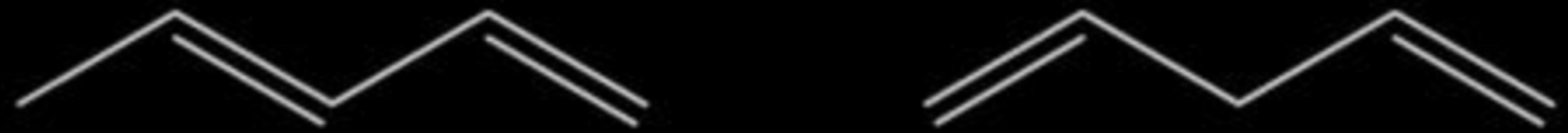
4.



12αH 9αH 6αH 6αH

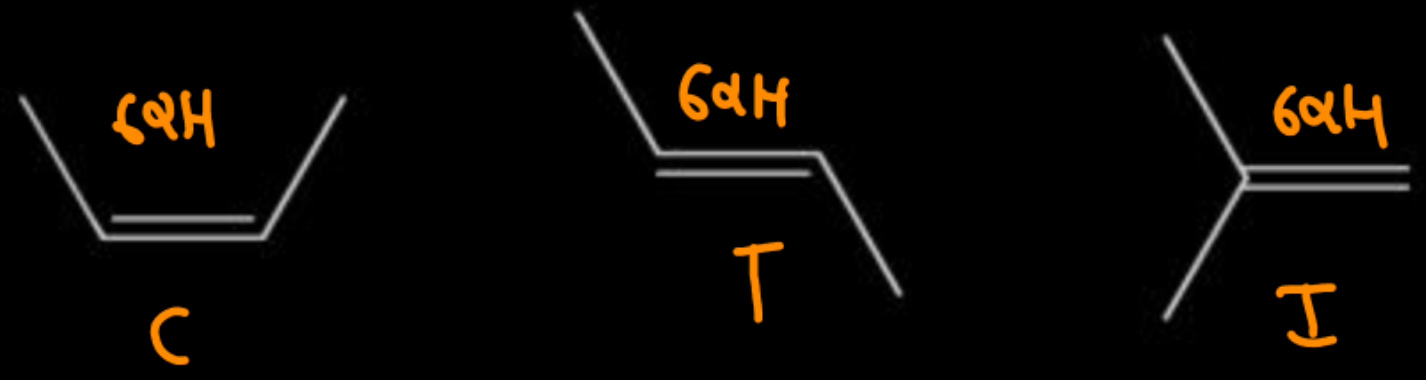
Stab → a > b > c > d
HOH → d > c > b > a

5.



Stab → a > b
HOH → b > a

6.



Stab → I > T > C

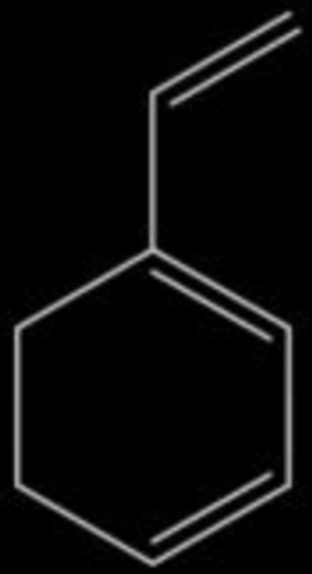
HOH → C > T > I

HOH → a > b > C

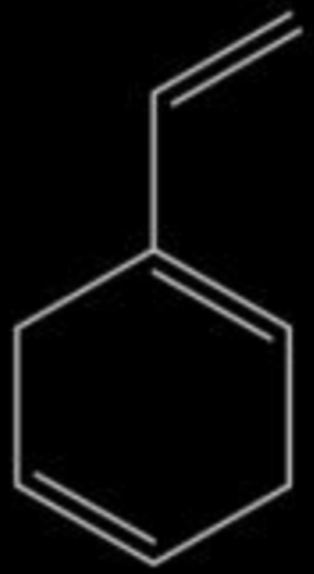
7.



Aromatic



NA
Reso more



NA
Reso less



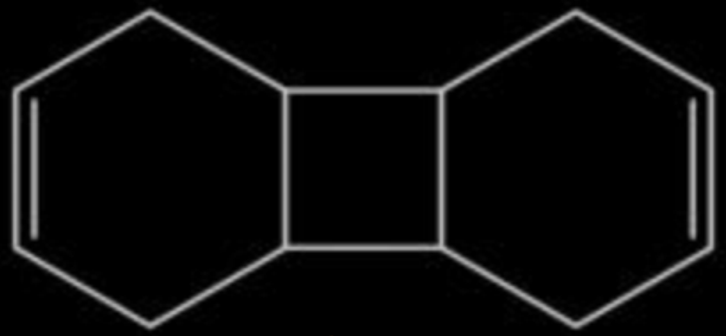
NA
Reso✗

Stab → a > b > c > d
HOH → d > c > b > a

8.



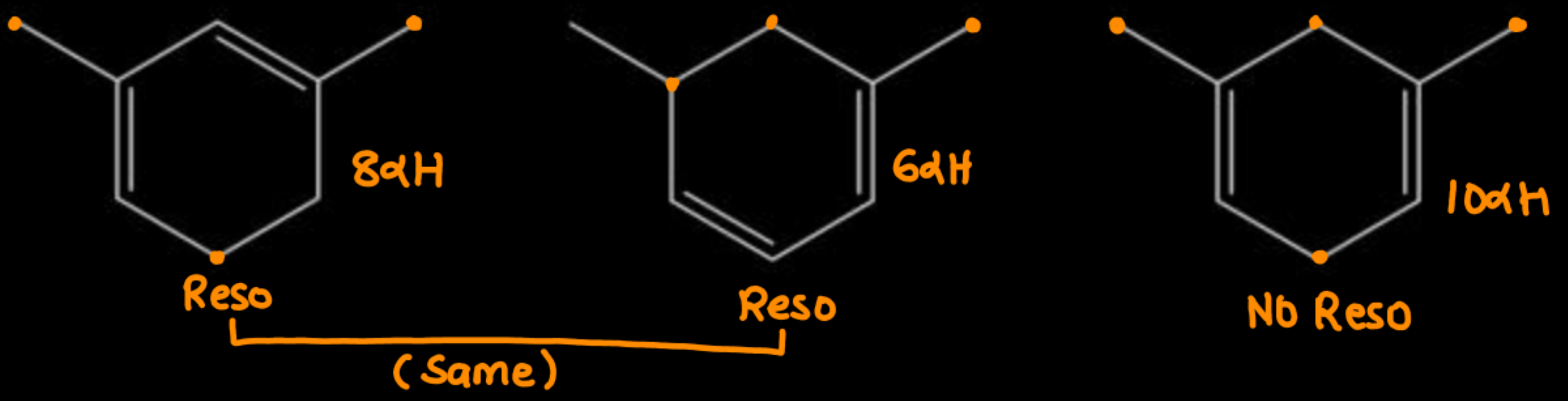
AA



NA

Stab → b > a
HOH → a > b

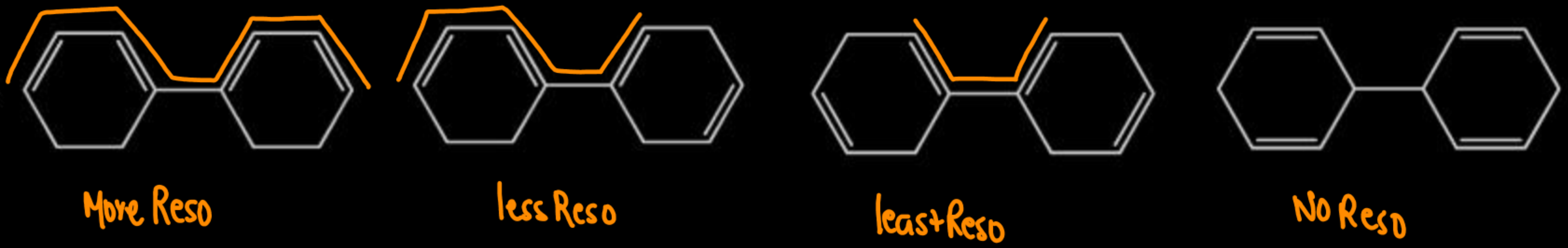
9.



Stab → a > b > c

HOH → c > b > a

10.



Stab → a > b > c > d

HOH → d > c > b > a

11. 

Reso | ResoX | ResoX 5αH | ResoX 8αH

Stab → (a & b) > (c & d)

Stab → a > b > d > c

HOH → (a & b) > (c & d)

→ b > a > c > d

12. 

HOH → a > b > c

Stab → a > b > c

Heat of Combustion (HOC)

Burning Hydrocarbon in presence of oxygen to produce CO_2 and H_2O is called combustion.

याद $\quad C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow x\,CO_2 + \frac{y}{2}H_2O$

$C_3H_8 + \left(3 + \frac{8}{4}\right)O_2 \longrightarrow 3CO_2 + \frac{8}{2}H_2O$

$5\,O_2 \qquad 4H_2O$

Heat of combustion is released.

Exothermic rxn

$\Delta H < 0$

$\Delta H = -ve$

* (1) HOC ∝ no of Carbon

if no of Carbon is same

* HOC ∝ $\frac{1}{\text{stability (2)}}$ ∝ branching (3)

1. 

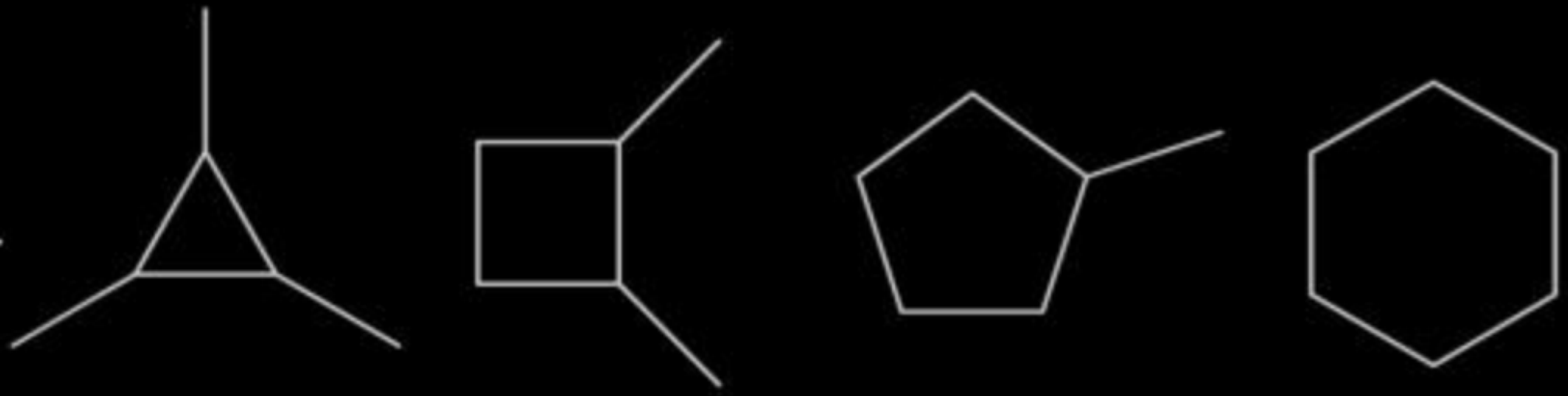
HOC → d > c > b > a

2. 

HOC → c > b > a

3. 

HOC → d > c > b > a

4. 

num of Carbon → Same

$HOC \propto \frac{1}{Stab}$

Stab → d > c > b > a

HOC → a > b > c > d

Size of Ring ↑ stability ↑ angle strain ↓

5.  

Stab → b>a
HOC → a>b

6. 

Reso ✓



Reso ✗

Stab → a>b
HOC → b>a

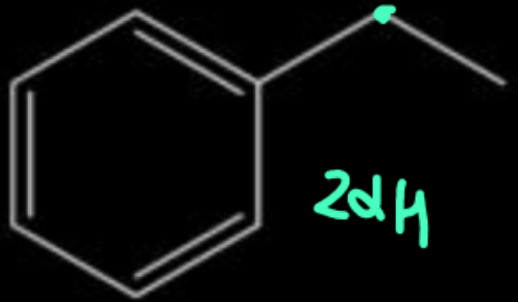
7. 

AA (Unstable)

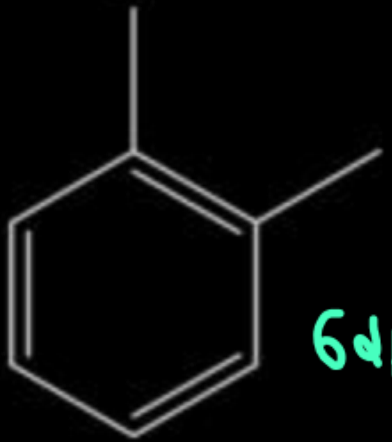


A (Stable)

Stab → b>a
HOC → a>b

8. 

2αH



6αH

Stab → b>a
HOC → a>b

9.   $CH_2{=}CH_2$

HOC → a>b>c

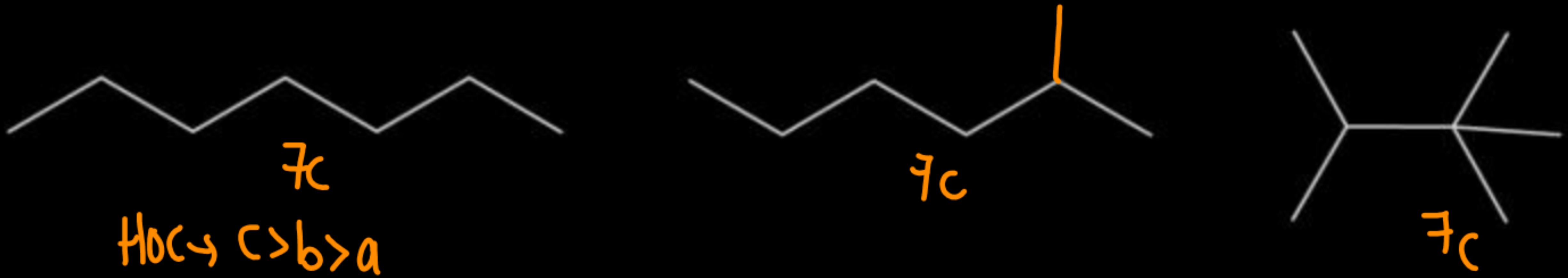
10. 

HOC → c>a>b

11. 

Stab → b>c>a

HOC → a>c>b

12. 

HOC → c>b>a

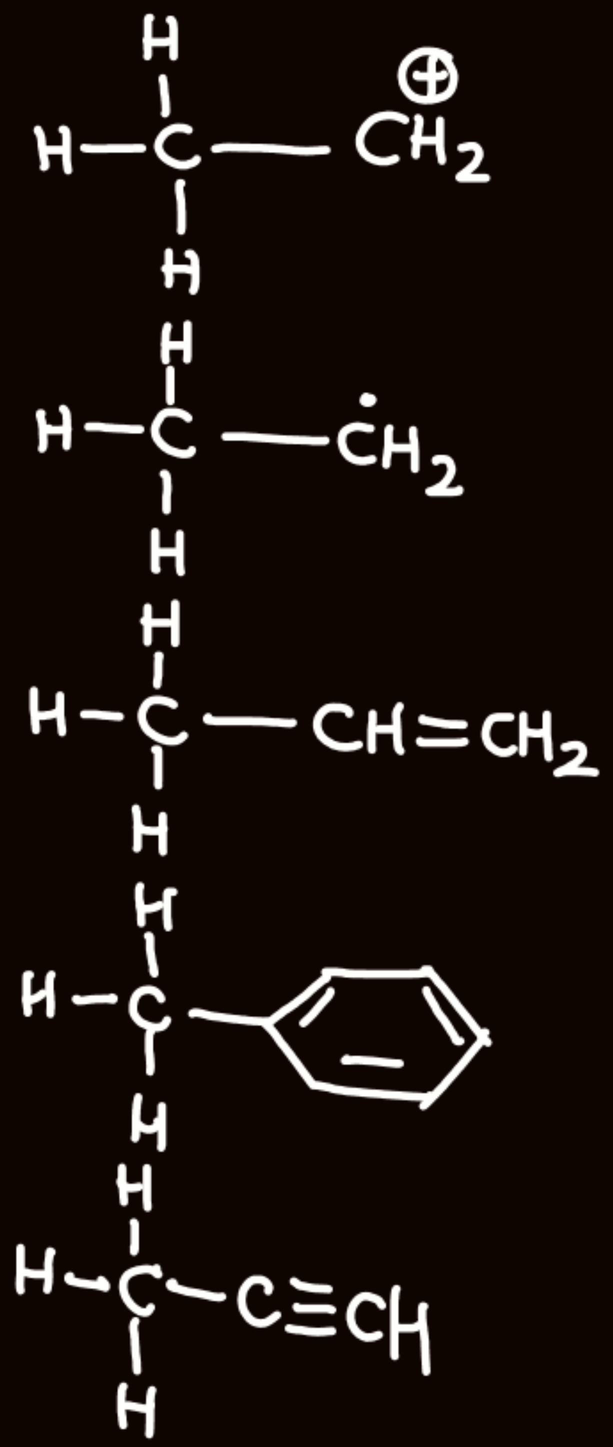
THANK YOU
All the Best!!

Hyperconjugation

Complete delocalisation of C–H (σ) Sigma electron with Vacant orbital of Carbocation.

Half filled orbital of Free Radical.

antibonding π^* (anti) molecular orbital of π bond.



Comparison b/w Resonance & Hyperconjugation

Reso	Hc
π σ ⊕	C–H σ ⊕
π σ ⊙	C–H σ ⊙
π σ (π)	C–H σ (π)

Baker–Nathan effect

No bond Resonance

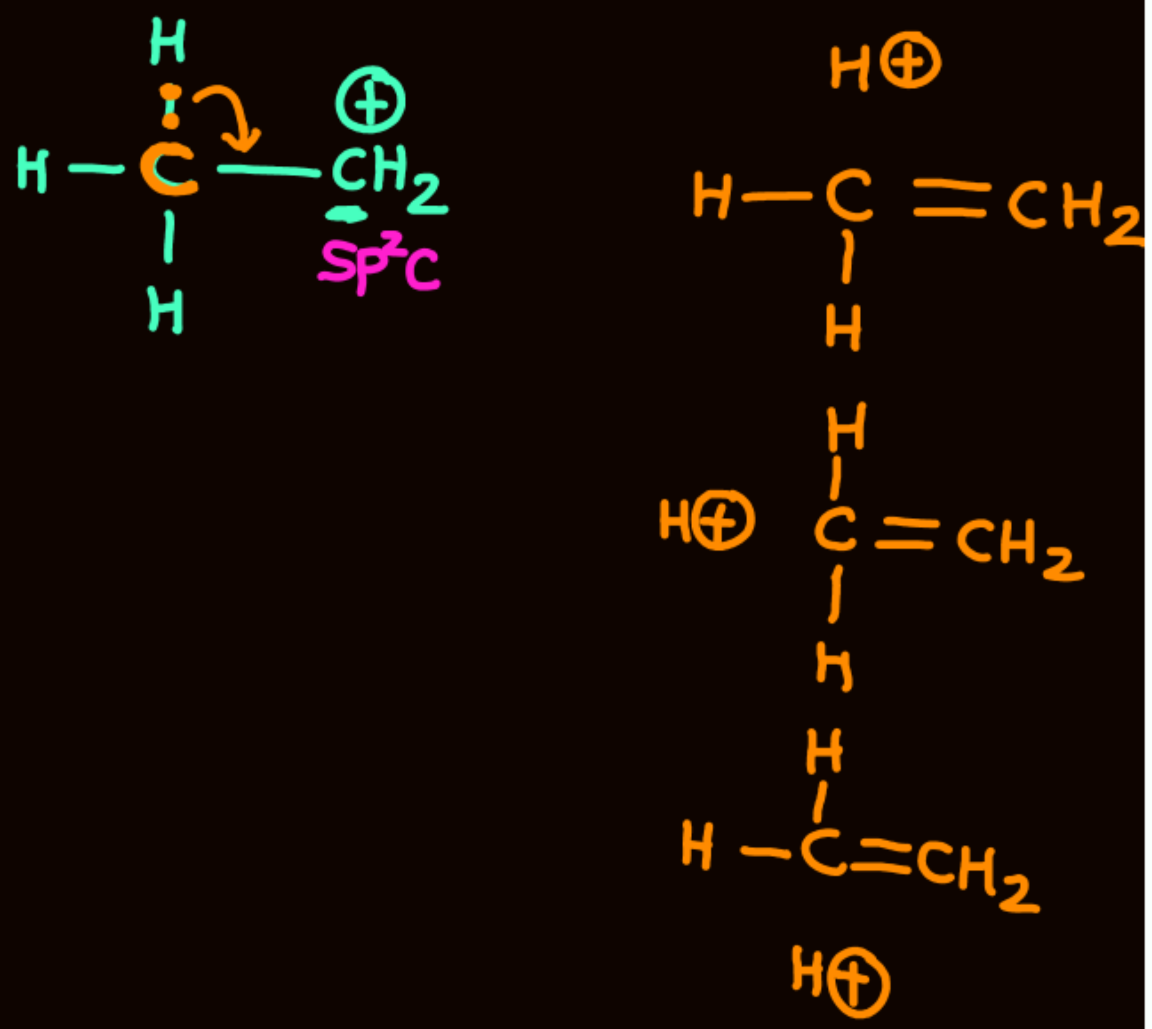
σ π Resonance

Hc never possible in Carbanion.

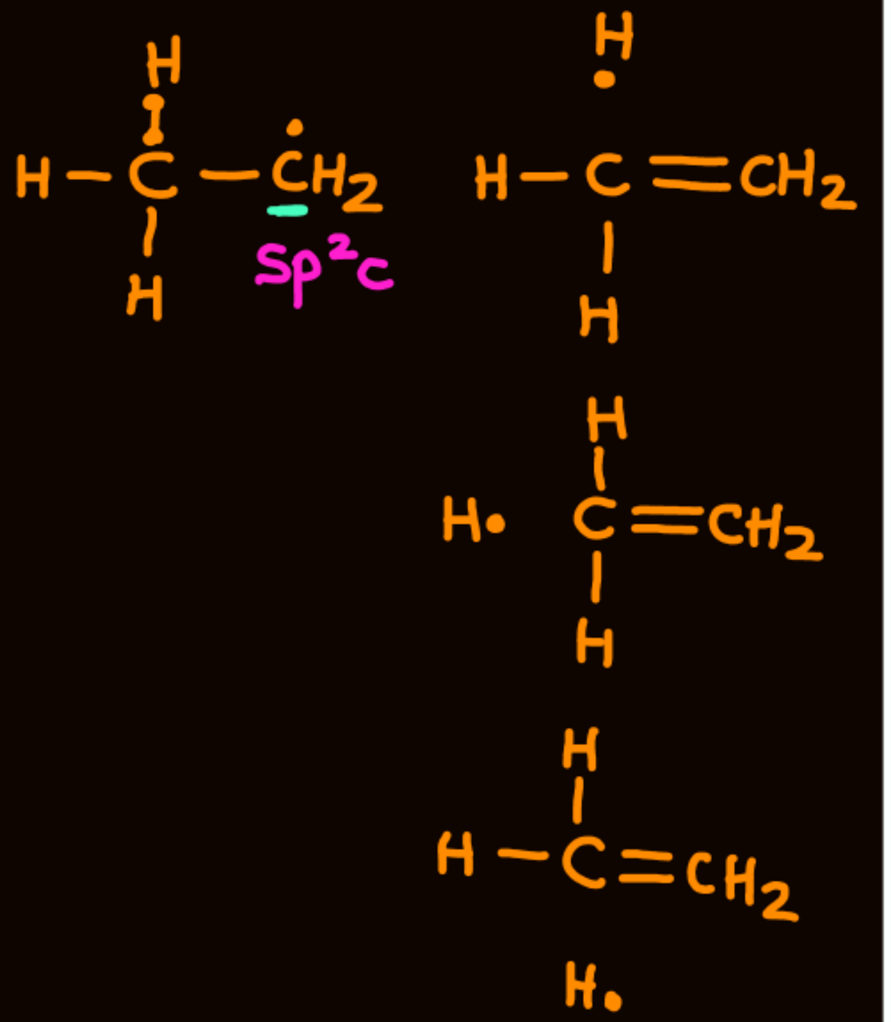
* permanant effect.

* Hc ↑ stability because +ve charge, free radical, π bond delocalises.

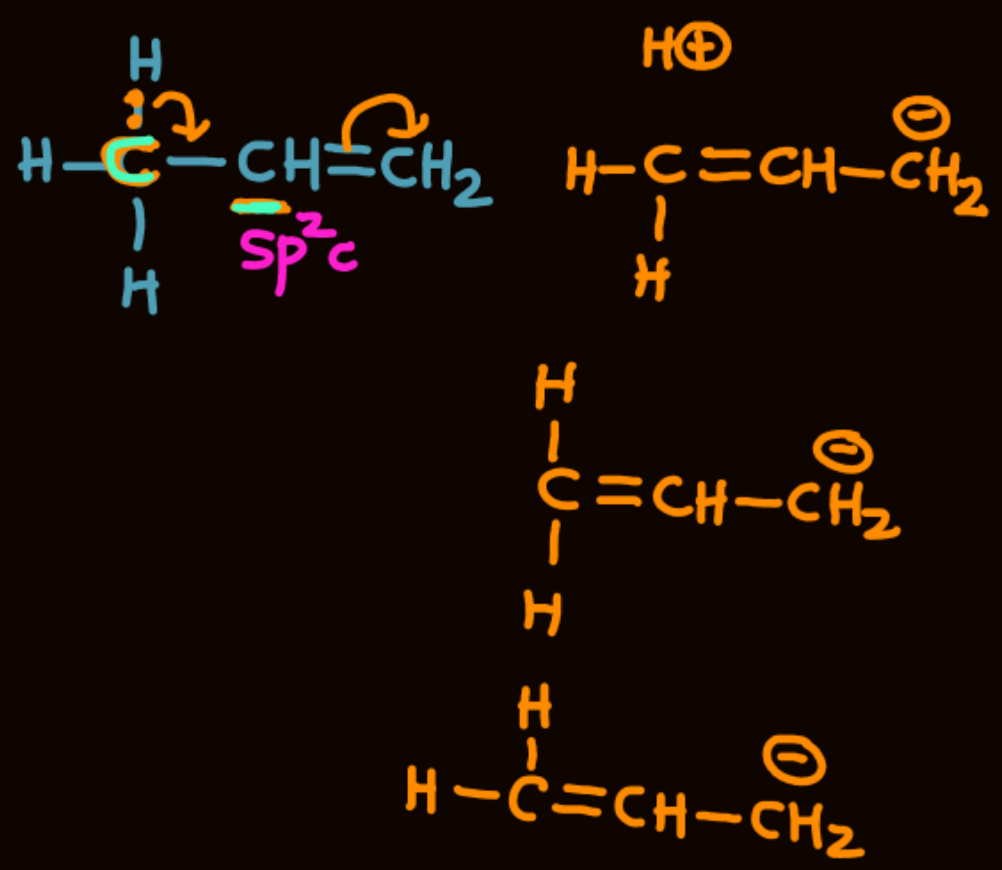
Hc in Carbocation



Hc in FreeRadical



Hc in π bond



* The Carbon directly attatched to carbocation, FreeRadical, π bond ⟶ "α" Carbon (must be sp^3)
* Hydrogen attatched to α Carbon is Called α Hydrogen.
* Num of αH = Num of Hyperconjugation.
* More αH ⇒ More Hyperconjugation ⇒ More Stability

VTS: sp/sp^2c से जुड़ा हुआ sp^3 carbon को α Carbon कहते हैं।

Condition of Hyperconjugation

Atleast 1 αH must be present with Carbocation, free Radical, π bond.

Q. Compounds/Ions which can show hyperconjugation.

(1) $CH_3^{\oplus}$ αC ✗ αH ✗ HC ✗

(2) $CH_3-CH_2^{\oplus}$ αC ✓ 3αH ✓ HC ✓

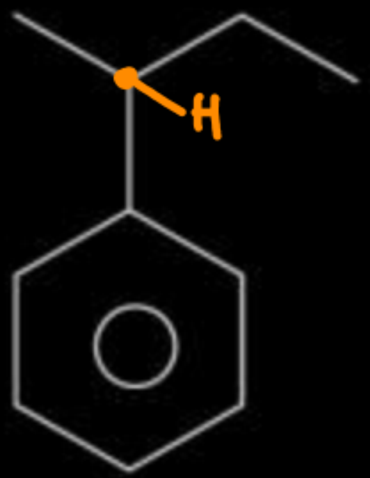
(3) $CH_2=CH_2$ αC ✗ αH ✗ HC ✗

(4) $CH_3-CH_2^{\ominus}$ ✗

(5) $CH_3-CH=O$ αC ✓ αC ✓ HC ✓

(6) 

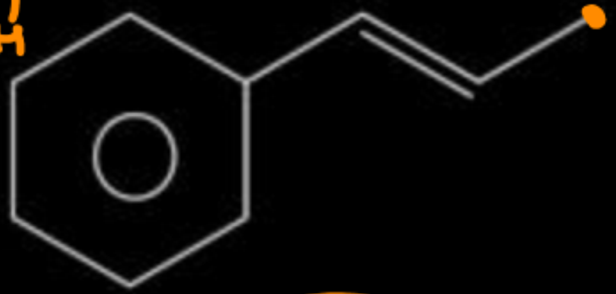
αC ✗ αH ✗ HC ✗

(7) 

αC ✓ 1αH ✓ HC ✓

(8) 

αC αH ✓ HC ✓

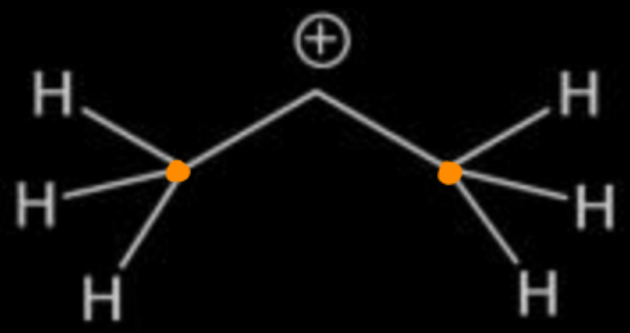
(9) 

αC ✓ 3αH ✓ HC ✓

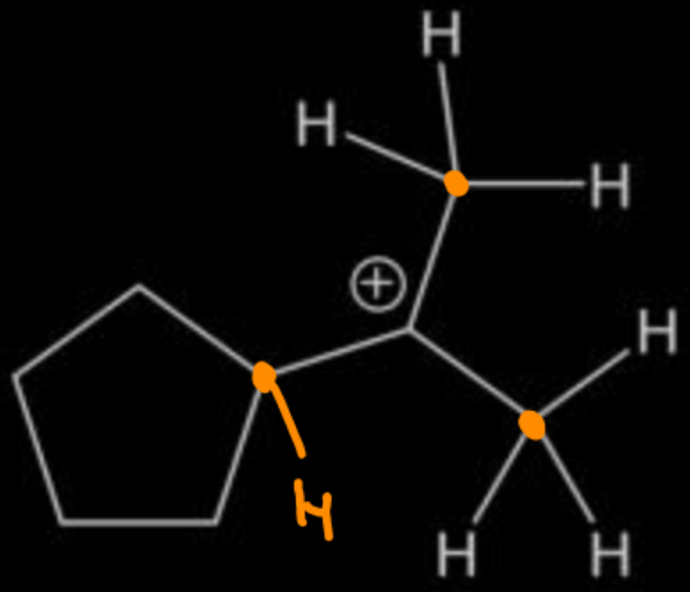
(10) $CH_3-C\equiv CH$

αC 3αH HC ✓

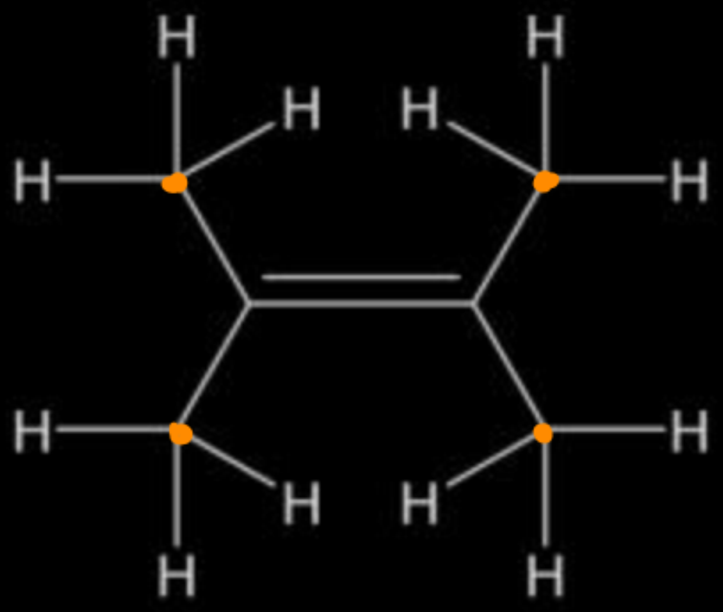
Q. Calculate the total number of $\alpha - H$.

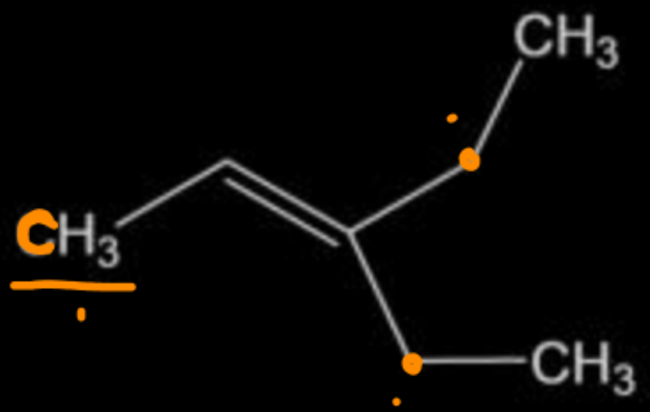
(1) 

→ 6α H

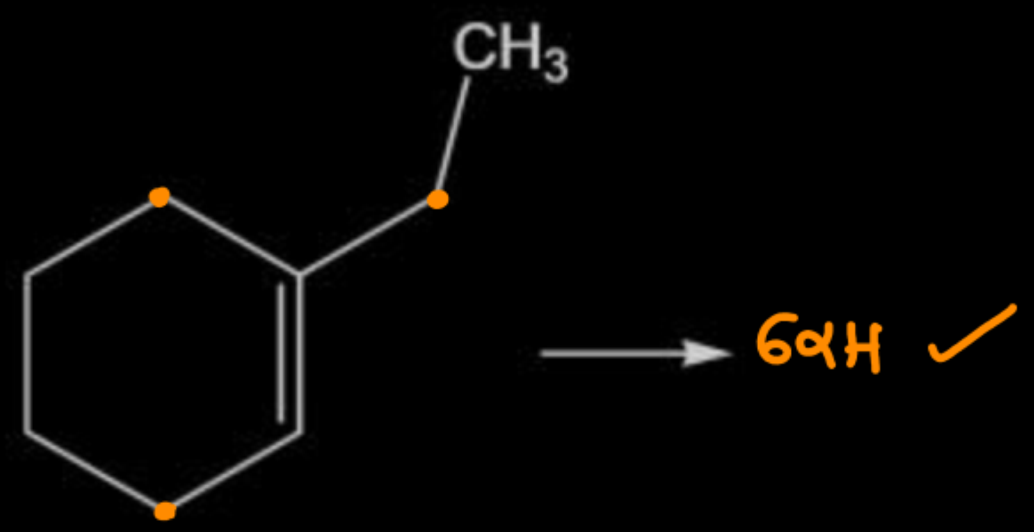
(2) 

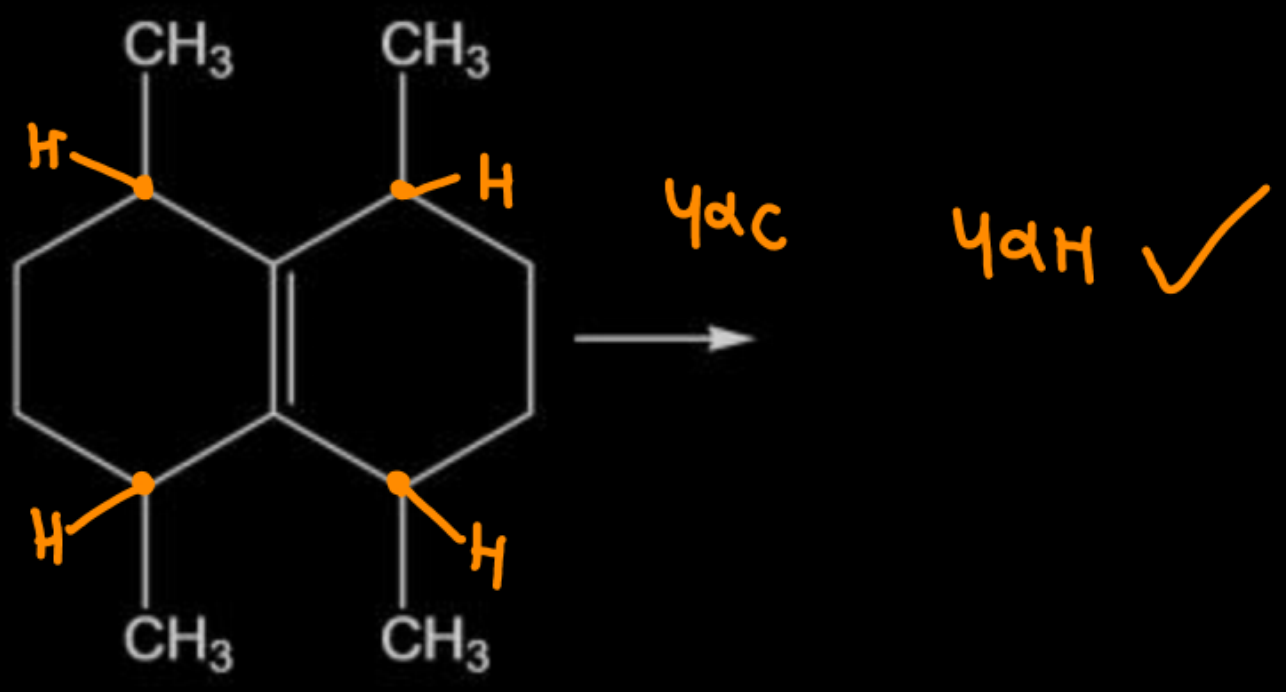
→ 7α H ✓

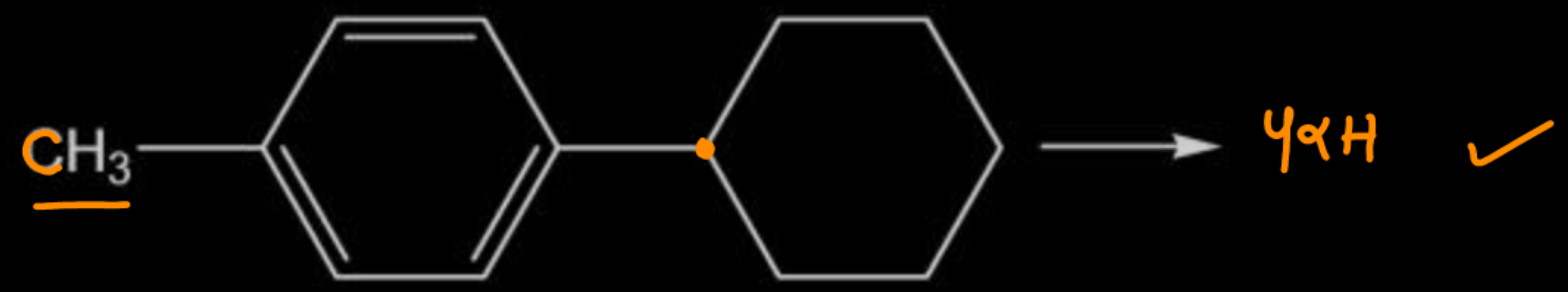
(3)  → 12αH ✓

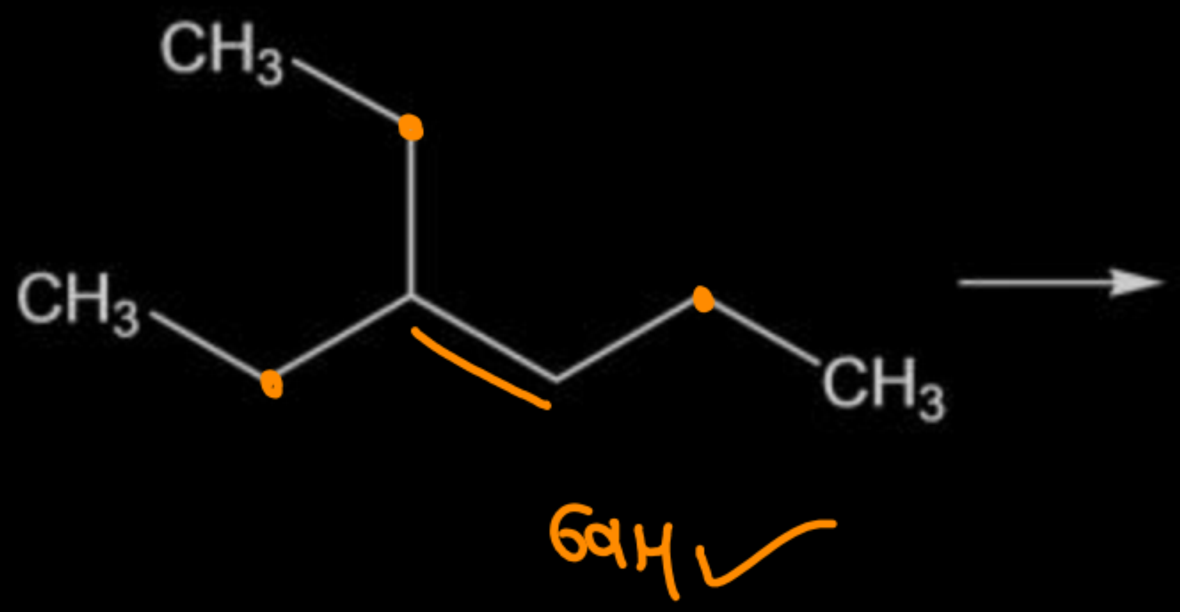
(4) 

→ 7αH ✓

(5) 

(6) 

(7) 

(8) 

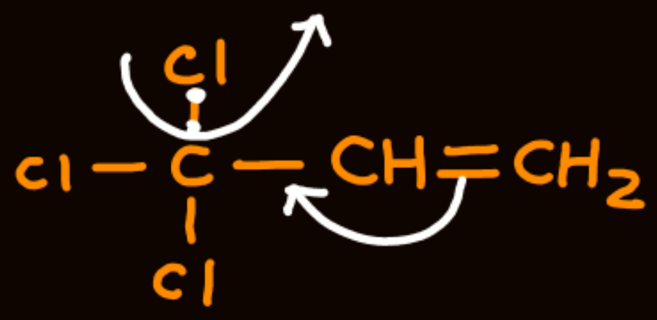
SOME Important points

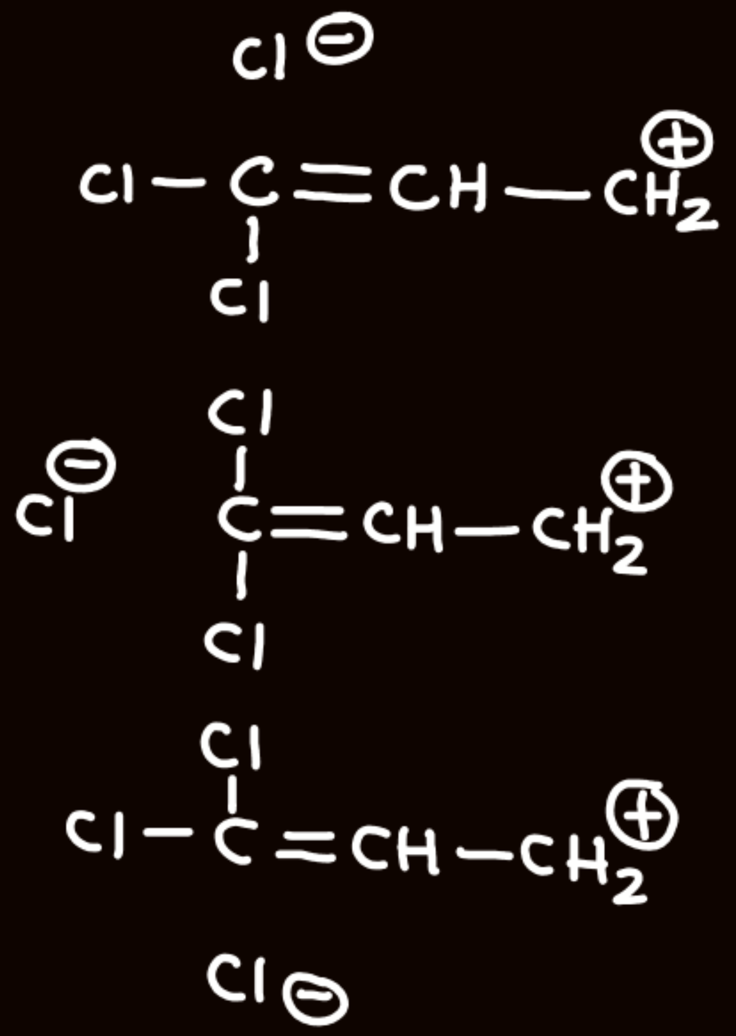
* Mesomeric > Hyperconjugation > Inductive (M > H > I)
  - Mesomeric → Strong Effect → π bond delocalise → easy
  - Hyperconjugation → σ bond delocalise → difficult
  - Inductive → weak effect

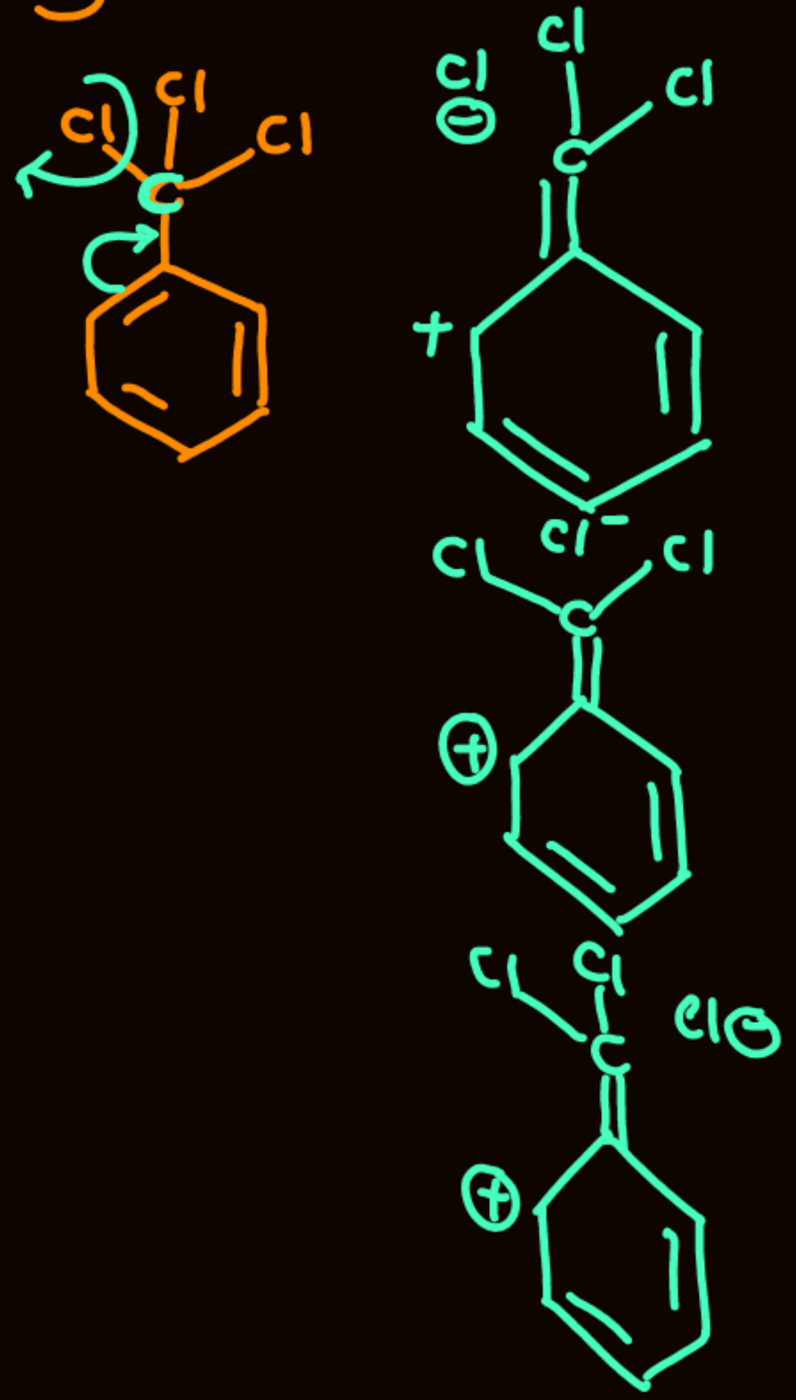
* Hyperconjugation
  - +H — donates C–H σ electron — EDG
  - –H — withraws e^- — EWG

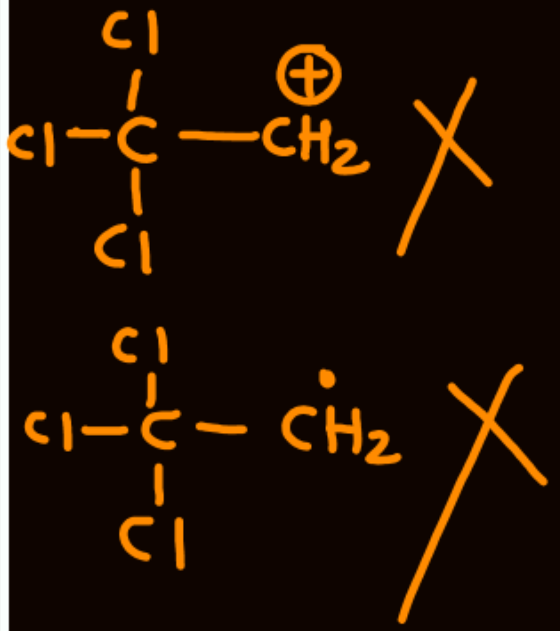
Reverse Hyperconjugation (–H)

only seen when π is in conjugation with $-CCl_3$.

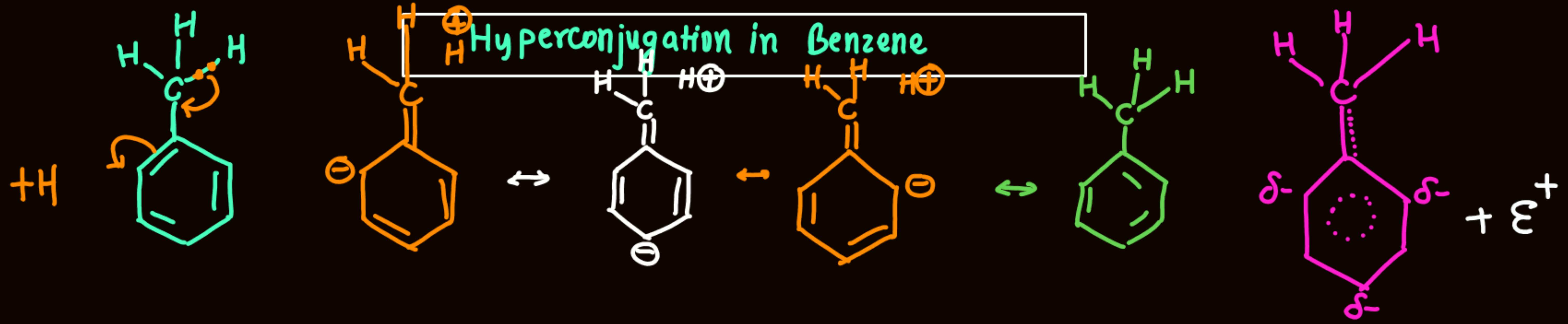


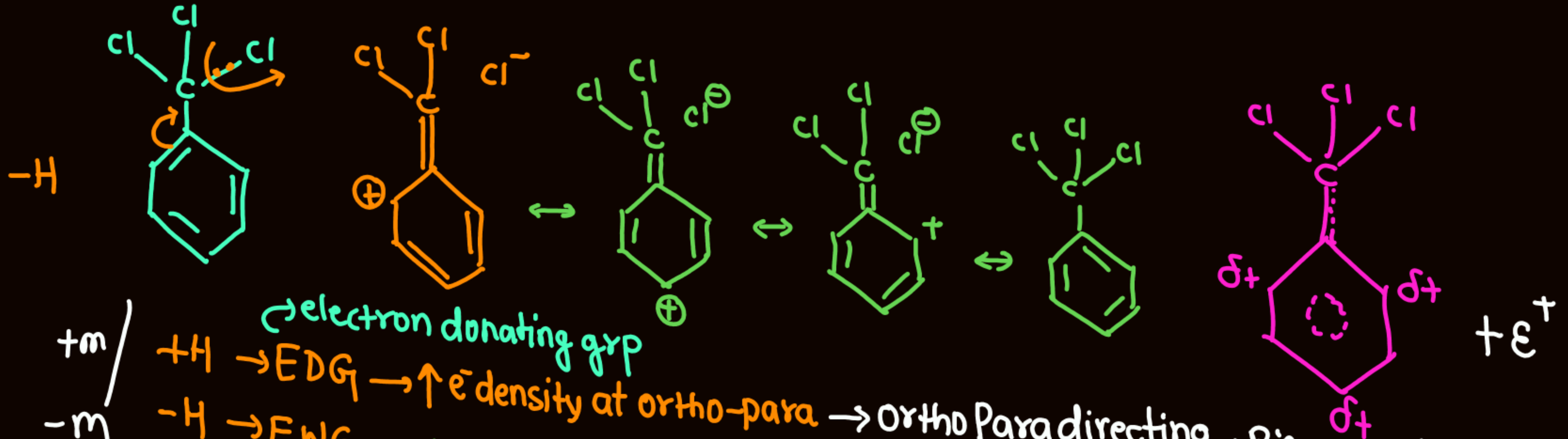






Hyperconjugation in Benzene





+m / −m

electron donating grp

+H → EDG → ↑ e^- density at ortho-para → ortho para directing → Ring activating group.

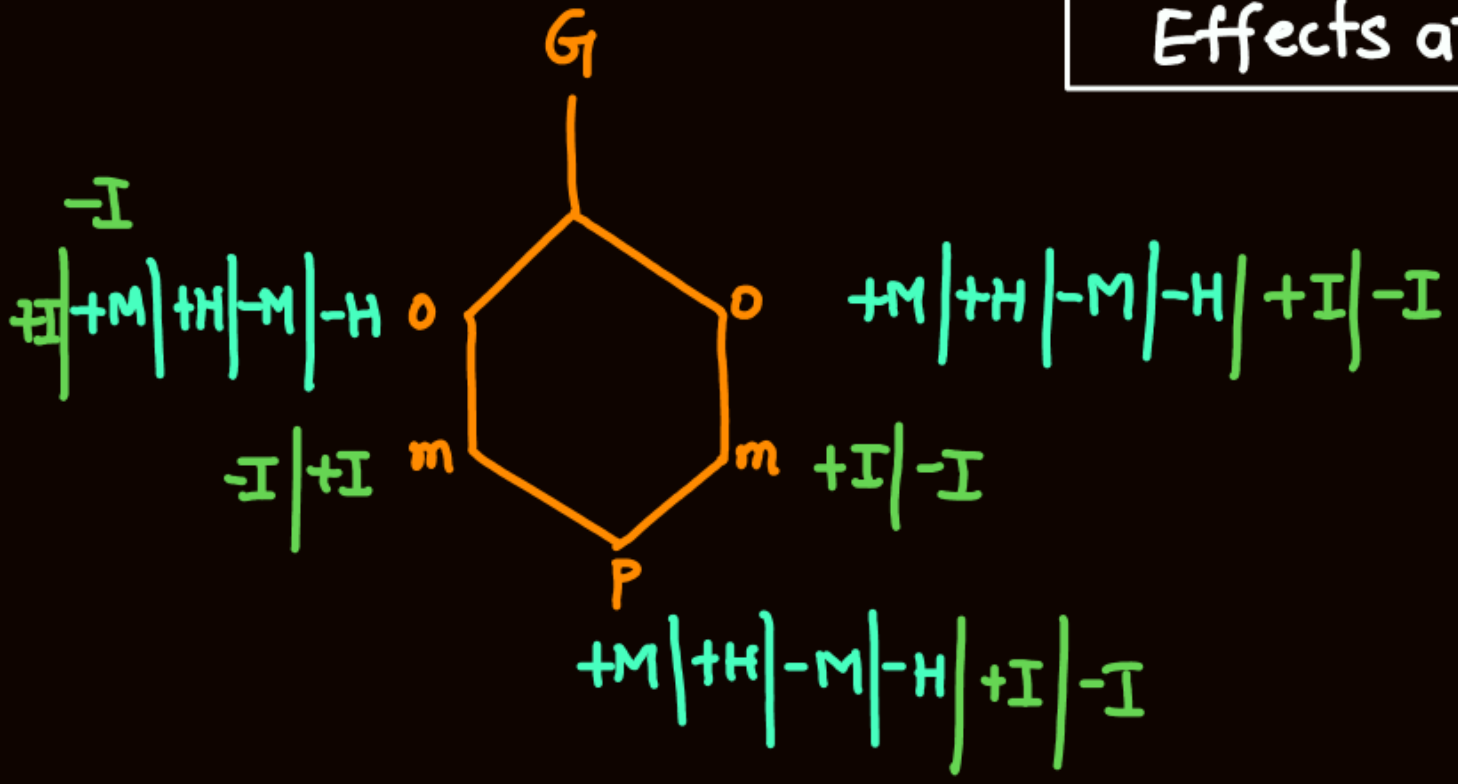
−H → EWG → ↓ e^- density at ortho-para → metadirecting → Ring deactivating group.

electron withdraw grp

$(HC)_{ortho} = (HC)_{para}$

distance independent

Effects at ortho/Para/Meta



Free Radical/Carbocation → M|H|I

Carbanion → m|I

Application of Hyperconjugation

Stability of Carbocation $\propto +H \propto \frac{1}{-H}$

Stability of freeradical $\propto +H \propto \frac{1}{-H}$

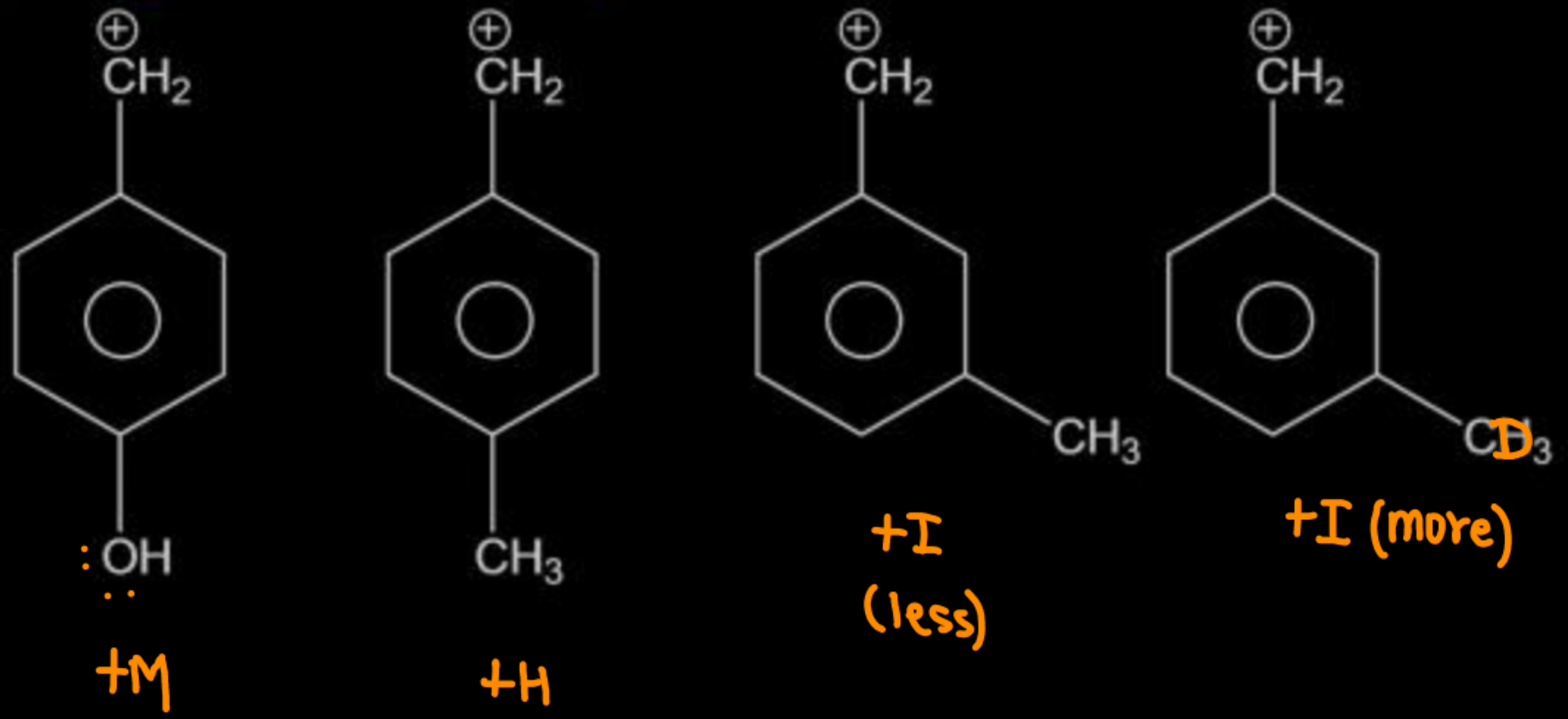
Stability of alkene $\propto$ num of αH

Basic strength $\propto$ Stab of Carbocation $\propto +H \propto \frac{1}{-H}$

Priority order → Fix → M/H/I

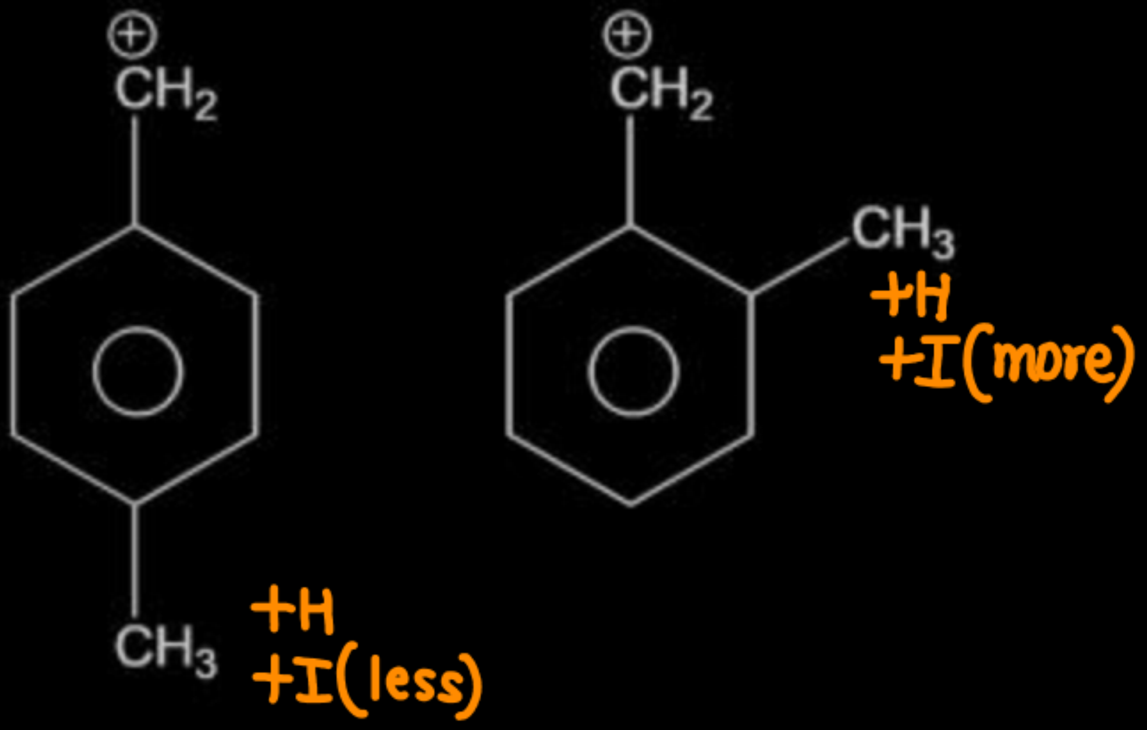
Q. Compare the stability of carbocation.

1.

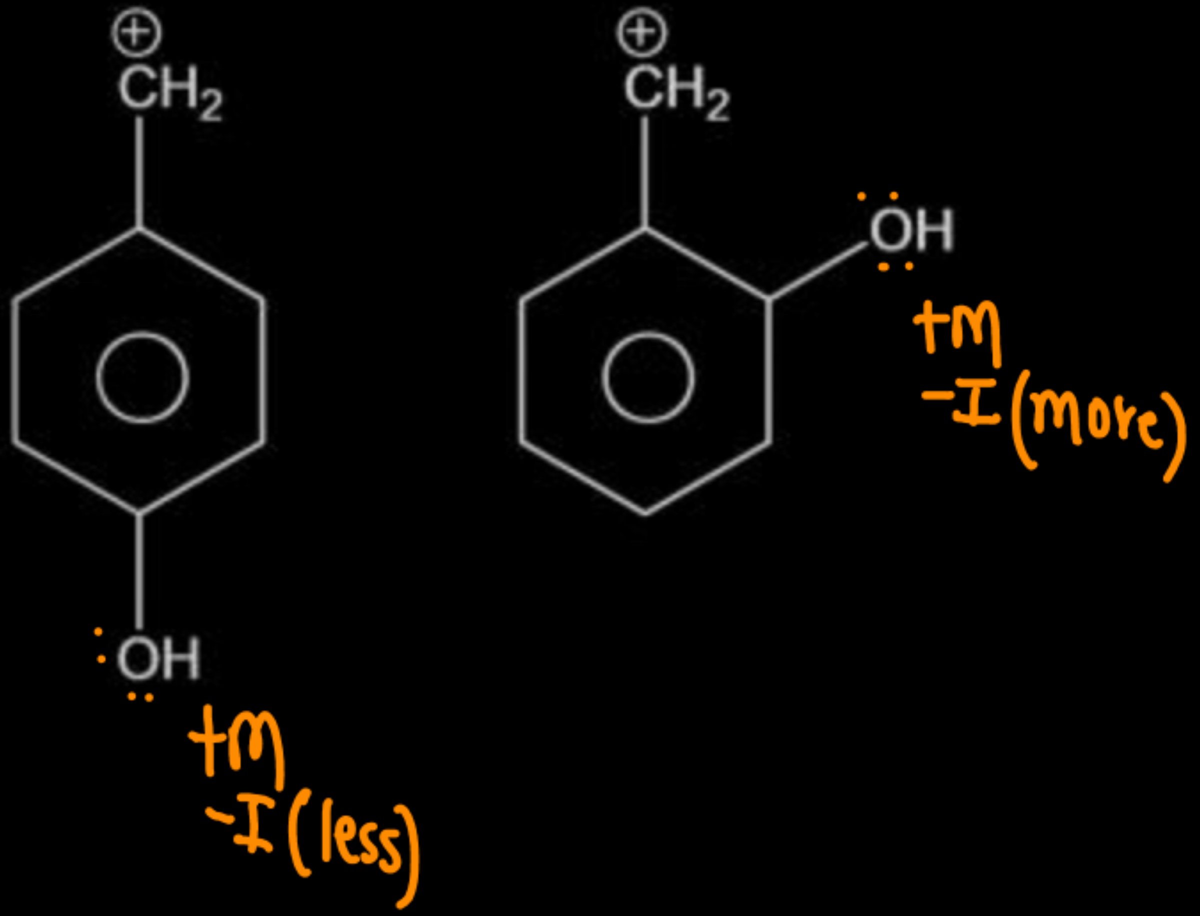


a > b > d > c

+I order → $-CT_3 > -CD_3 > -CH_3$

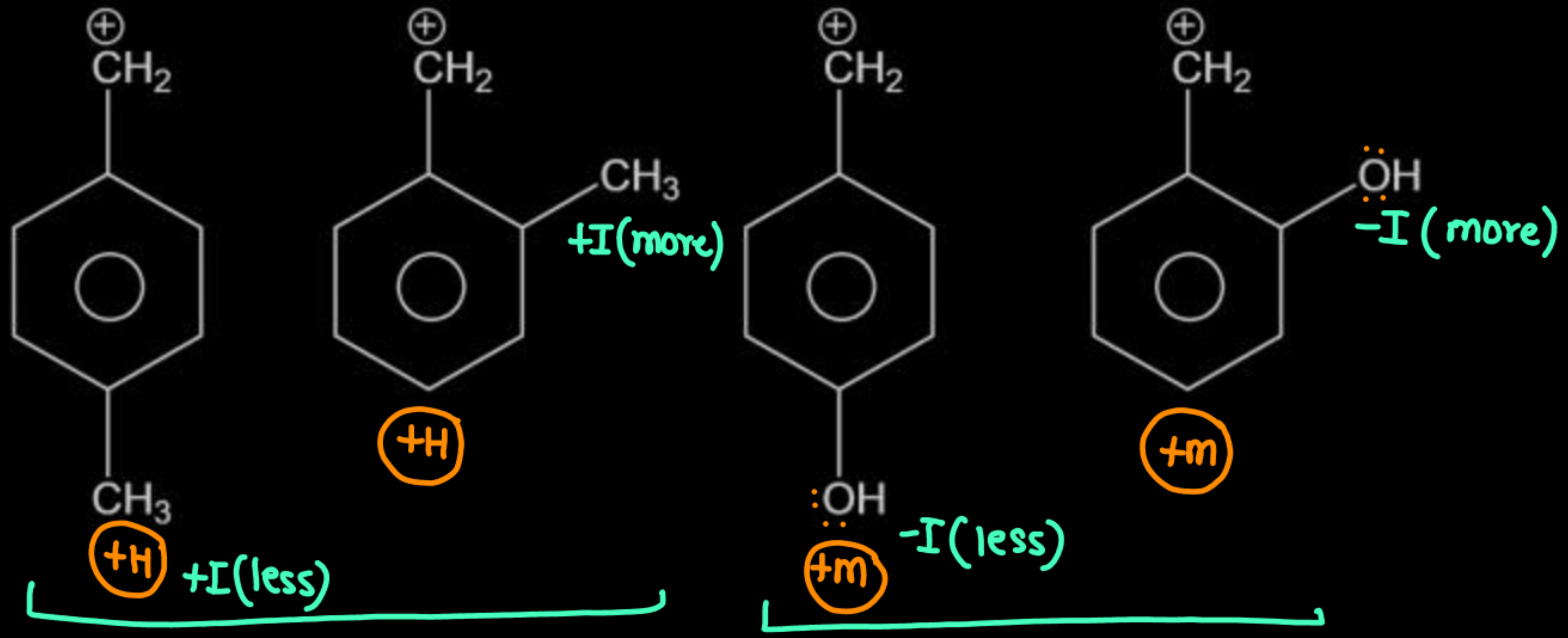
2. 

b>a

3. 

a > b

4.



3 & 4 > 1 & 2

3>4>2>1

THANK YOU

All the Best!!

Dancing Resonance / sigma Resonance



Cyclopropane

4σ bond

sp^3 Carbon

(109.5°)

Bondangle → 60°

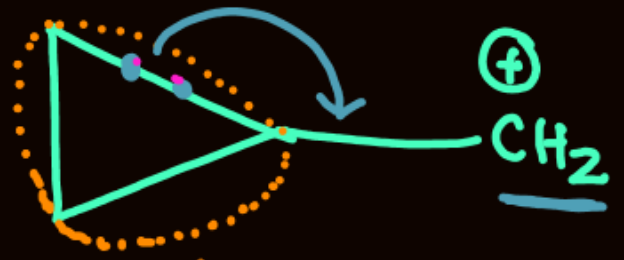
Cyclopropane → angle strain

→ Repulsion

→ Unstable

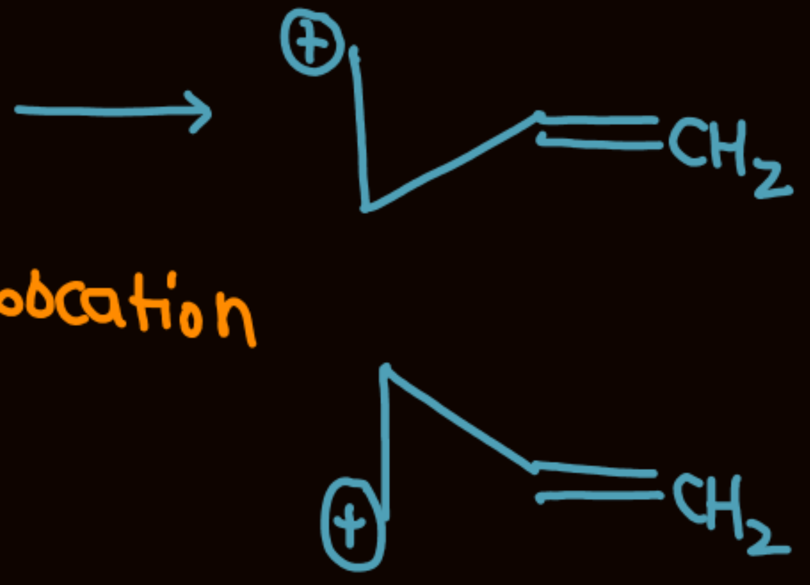


→ so it exist like this



cyclopropyl methyl carbocation

(CPM cation)



* In CPM cation C–C single bond acts as C=C.
* CPM cation becomes stable by dancing Reson (sigma Reson)

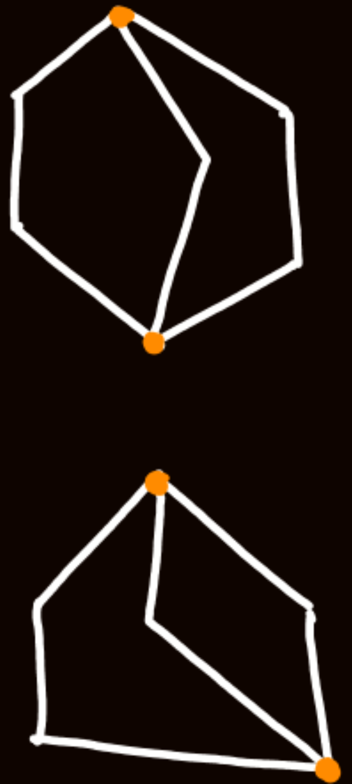
Bredt's Rule

It is applicable → Bridged Bicyclo Compounds & not applicable in Fused Bicyclo Compounds.

Bicyclo



Fused Bicyclo



Bridged Bicyclo

A/c to Bredt's Rule Bridge Head Carbon cannot be sp²/ planar/ +ve charge/ free Radical/ π bond.



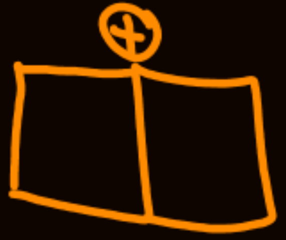
donot exist



donot exist



donot exist



exist ✓

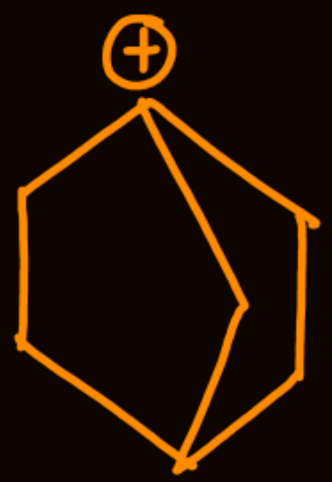


exists



donot exist

__note__ A/c to bredt's Rule if one Ring becomes 8 member or higher then Bridgehead carbon can have +ve charge, Free Radical, π bond, planar (exist).



donot exist



exist

Stability of Intermediate

Stab of Carbocation

1. B·B (BackBonding) → pπ-pπ Reso; → pπ-dπ Reso
2. Dancing Reso → CPM cation
3. +ve charge → Part of aromatic
4. Amount of Resonance
5. Hybridisation → +ve charge on less EN is stable & -ve charge on more EN is Stable.
6. +M
7. +H
8. +I
9. -I
10. -H
11. -M
12. +ve charge is a part of AntiAromatic

Stab of Carbanion

1. B·B (BackBonding) → pπ-pπ Reso; → pπ-dπ Reso
2. -ve charge → part of Aromatic
3. Amount of Resonance
4. Hybridisation → -ve charge Stable on more EN atom & +ve charge Stable on less EN.
5. -M
6. -I
7. +I
8. +M
9. -Ve charge → Part of anti aromatic

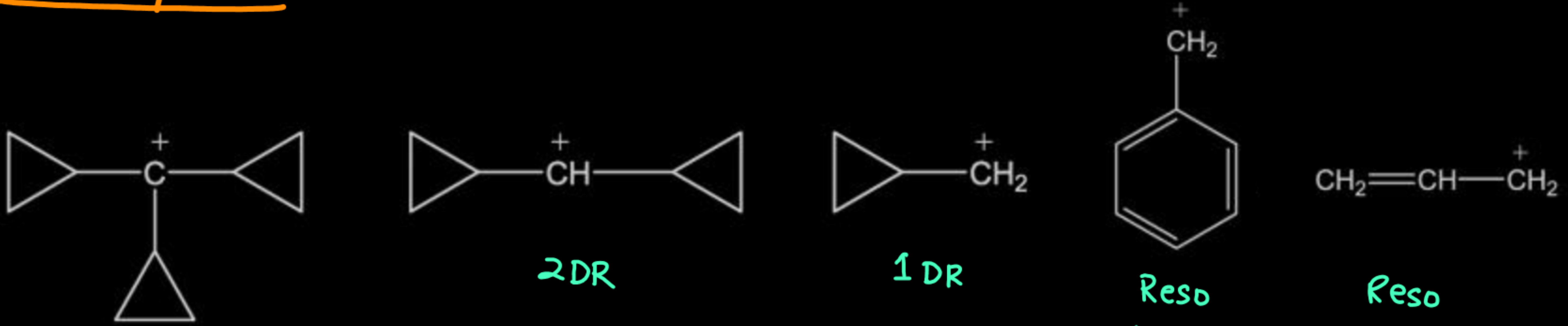
Stab of Free Radical

1. Amount of Resonance
2. Hybridisation → +ve charge/free radical is Stable on less EN.
3. +M
4. +H
5. +I
6. -I
7. -H
8. -M

stability order –

a>b>c>d>e

Q1.

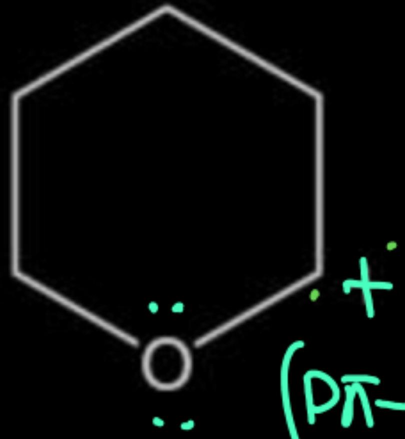


3 DR | 2 DR | 1 DR | Reso more | Reso (less)

Q2.

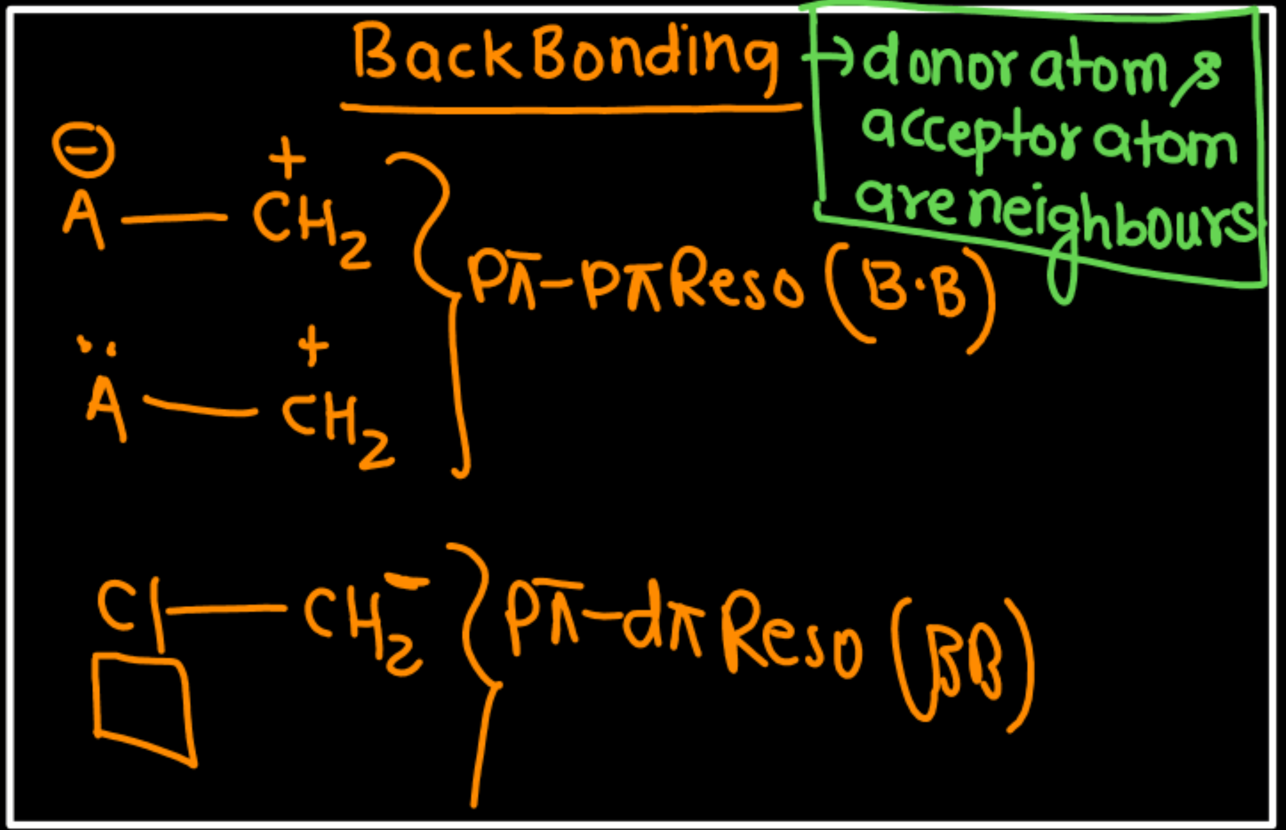


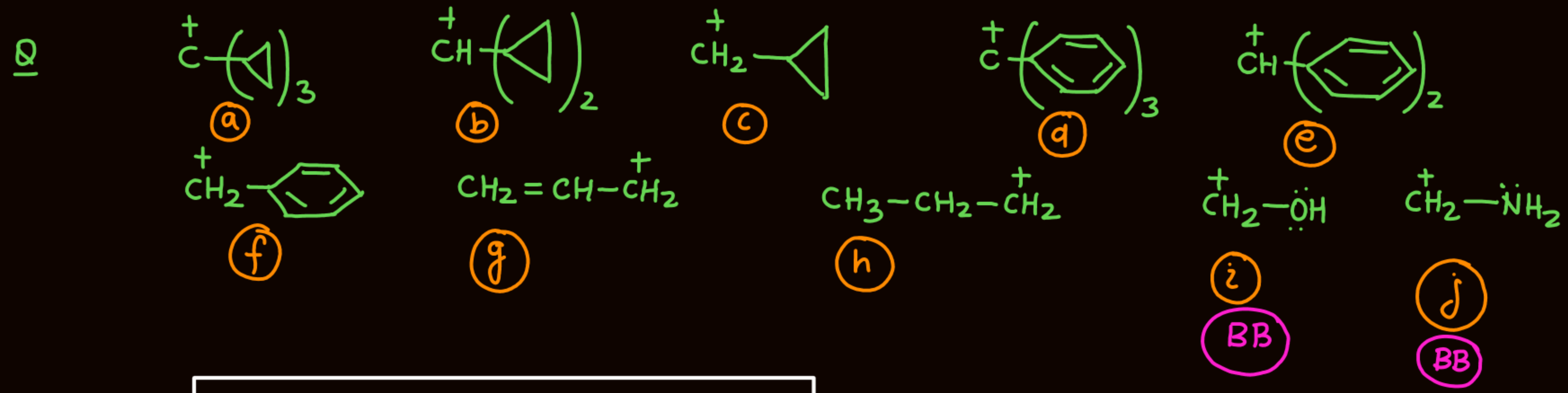
DR



(pπ–pπ Reso) BB

b>a





j > i > a > b > c > d > e > f > g > h

Q3. $CH_3-\overset{+}{C}H_2$ $\quad$ $CH_3-\overset{+}{C}H-CH_3$ $\quad$ $CH_2=CH-\overset{+}{C}H_2$ $\quad$ $Ph-\overset{+}{C}H_2$

3αH $\quad$ 6αH $\quad$ less Reso $\quad$ more Reso

d>c>b>a

Q4. $CH_2=CH-\overset{-}{C}H_2$ $\quad$ $CH_2=\overset{-}{C}H$ $\quad$ $CH_3-\overset{-}{C}H_2$

Reso $\quad$ More En $\quad$ less En

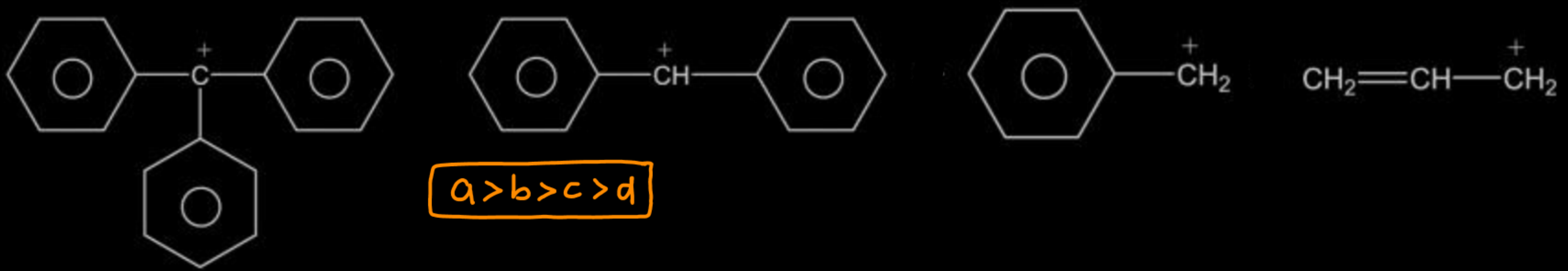
a>b>c

Q5. $CH_2=CH-\overset{+}{C}H_2$ $\quad$ $CH_3-\overset{+}{C}H_2$ $\quad$ $CH_2=\overset{+}{C}H$

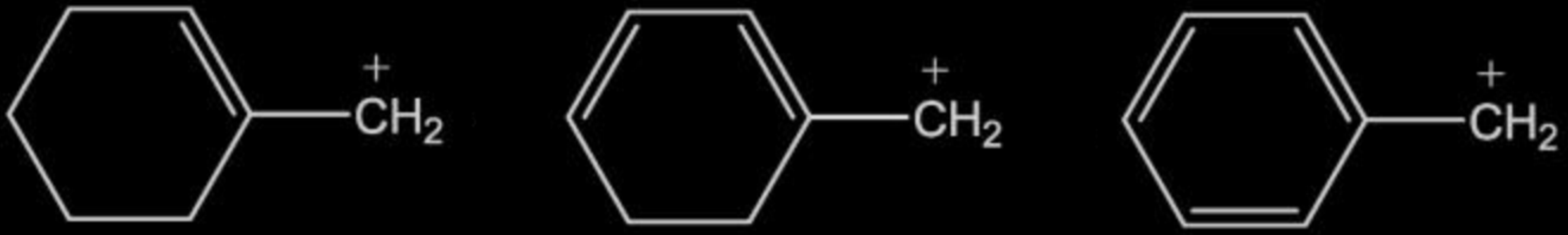
a>b>c

Reso $\quad$ 3αH $\quad$ +ve on More En → Unstable

Q6.

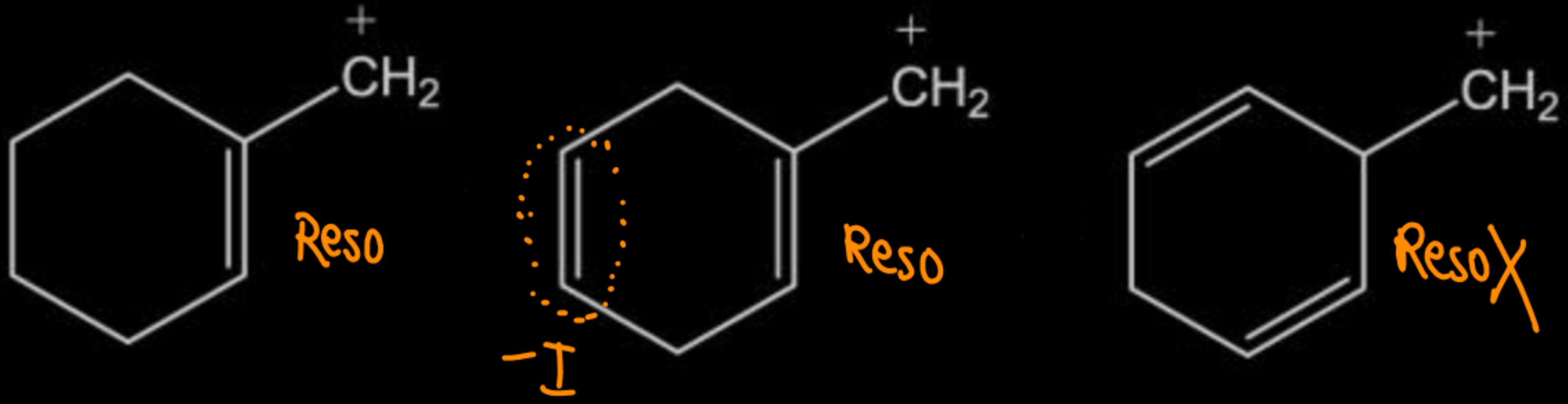


Q7.



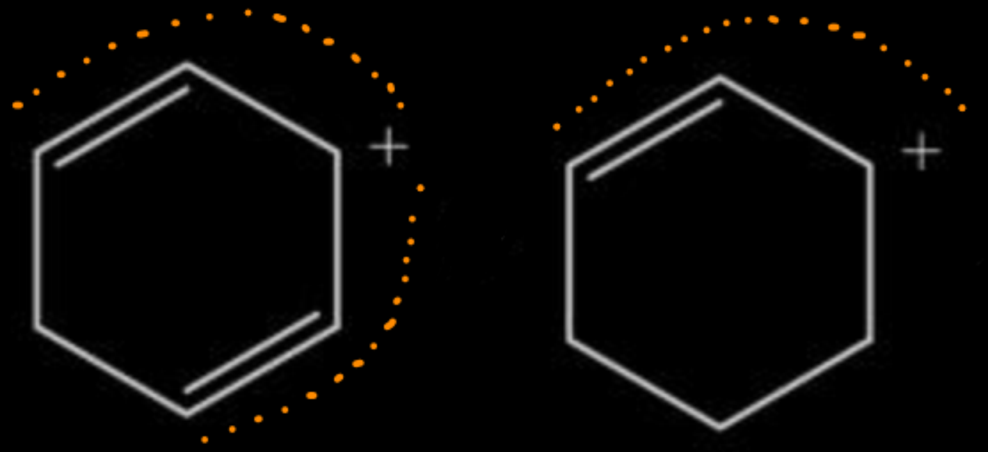
c>b>a

Q8.



a>b>c

Q9.



→ +ve charge → Unstable
↳ on more EN

→ +ve charge is not in Resonance

a > b > c

Q10.

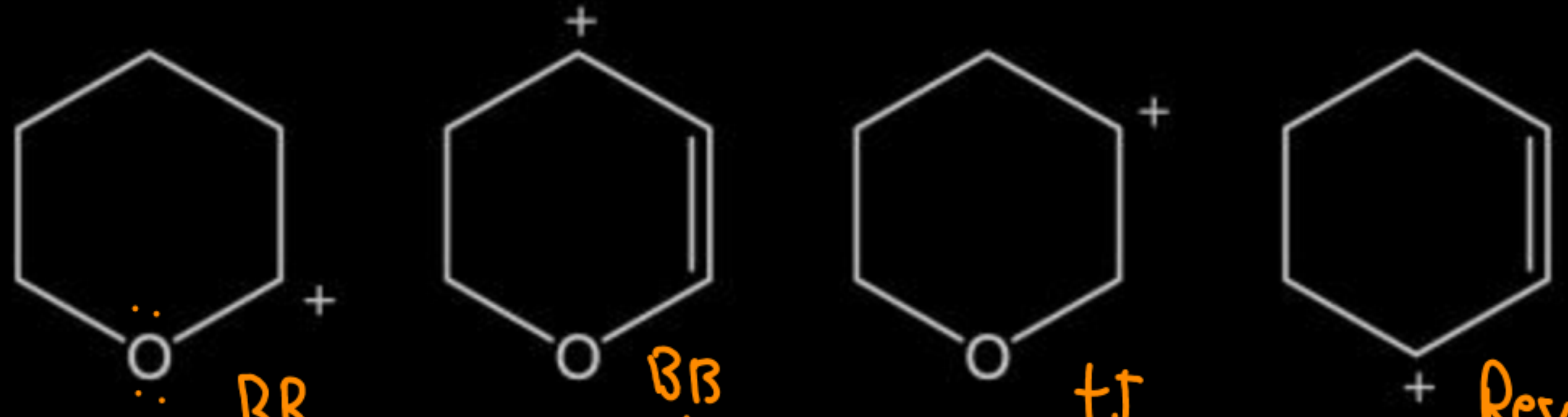


(a) (b) Reso (c) Reso (more) (d) no Reso

→ –ve charge → stable
↓
more EN

c > b > d > a

Q11.



(a) BB (b) BB + Reso (c) +I (d) Reso

b > a > d > c

$CH_2 = \overset{O^+}{\overset{|}{C}} - H$ (unstable)

Q12. $\overset{+}{C}H_2 - \overset{O}{\overset{\|}{C}} - H$ (no Reso) −I

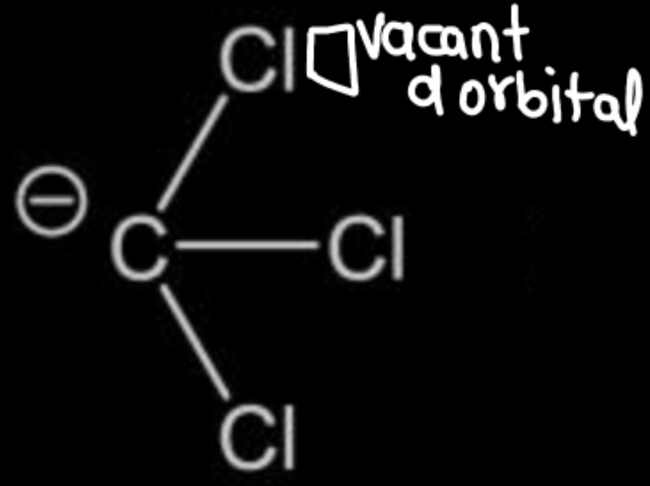
$\overset{+}{C}H_2 - CH_2 - \overset{O}{\overset{\|}{C}} - H$ (+I on CH_2, −I on $C(=O)H$)

b > a

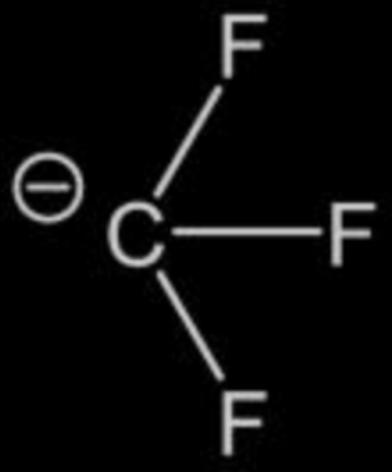
Q13. $CH_3 - \ddot{O} - \overset{+}{C}H_2$ (BB) $\quad Ph - \overset{+}{C}H_2$ (Reso) $\quad CH_3 - \overset{+}{C}H - CH_3$ (6αH) $\quad \overset{+}{C}H_2 - \underset{O}{\underset{\|}{C}} - CH_3$ (−I)

a > b > c > d

Q14.



BB



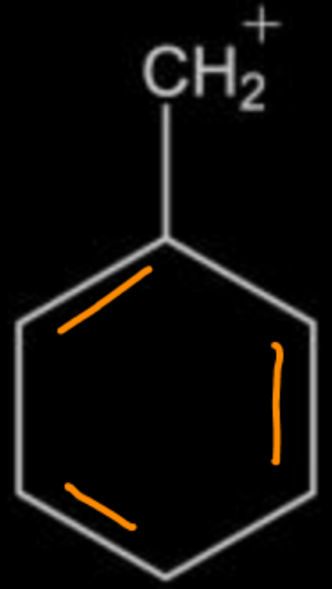
no BB

a > b

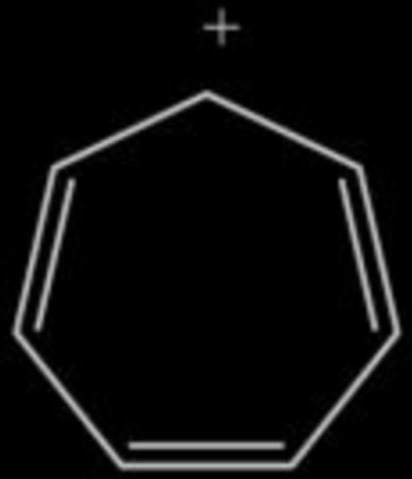
Q15.



AntiAromatic



normal Resonance



+ve charge is part of Aromatic

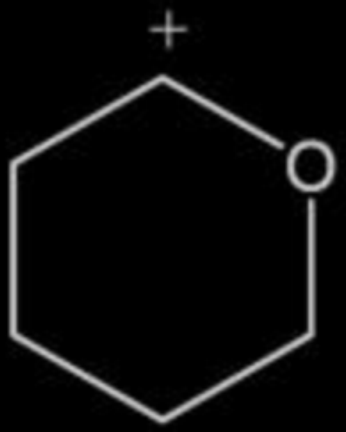
c > b > a

Q16. $Ph_3\dot{C}$ $Ph_2\dot{C}H$ $Ph\dot{C}H_2$

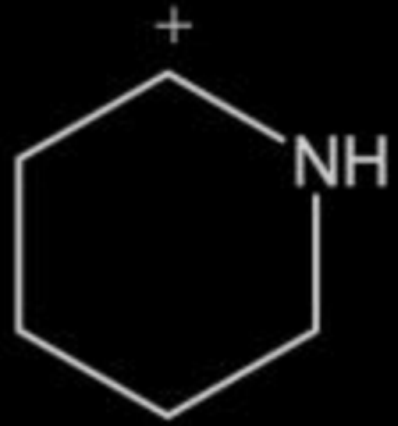


a > b > c > d

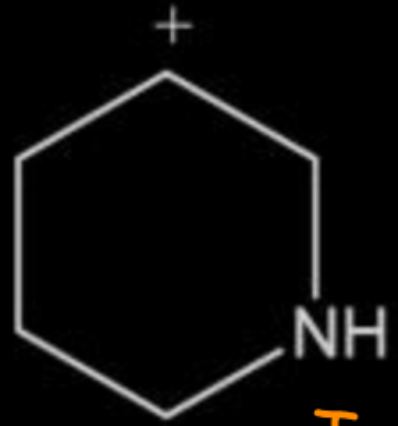
Q17.



(a) B.B.



(b) BB (more)



-I (less)

(c)

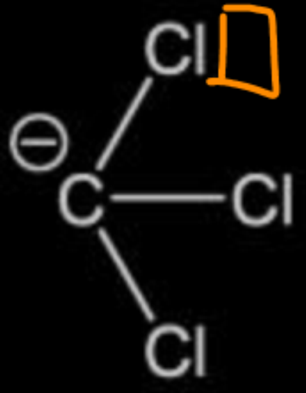


-I (more)

(d)

b > a > c > d

Q18.



BB



Reso

$CH_3-CH_2-CH_2^{\ominus}$

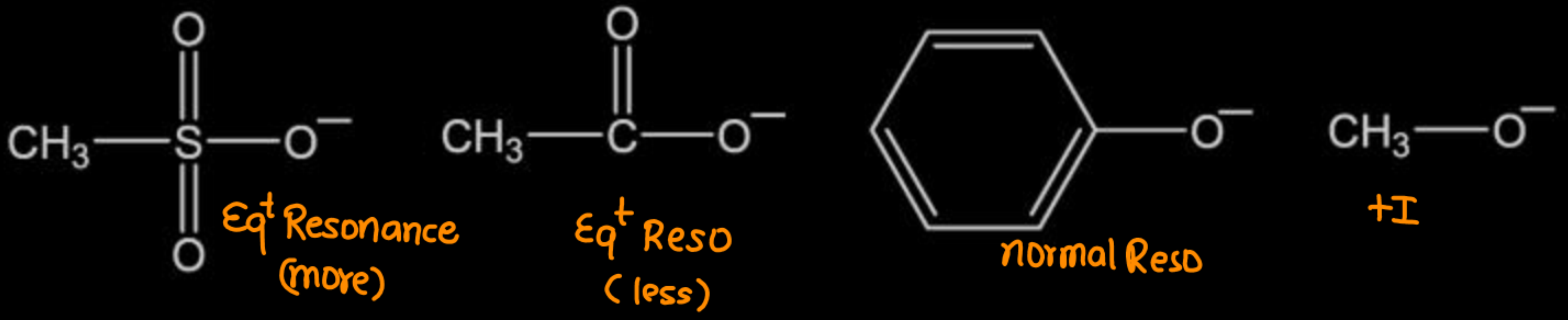
+I

a > b > c

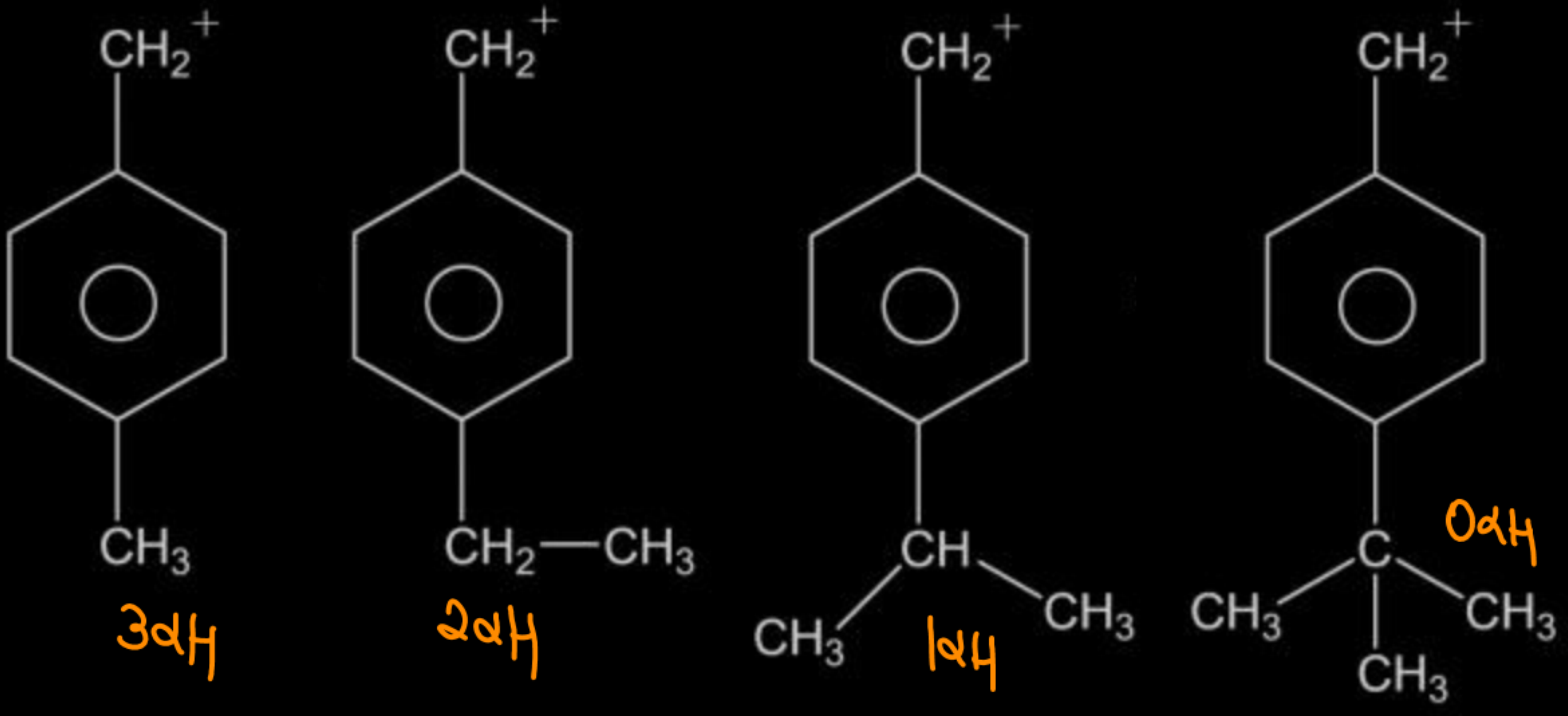
a>b>c>d

Eq+ Reso is more stable than normal Reso.

Q19.

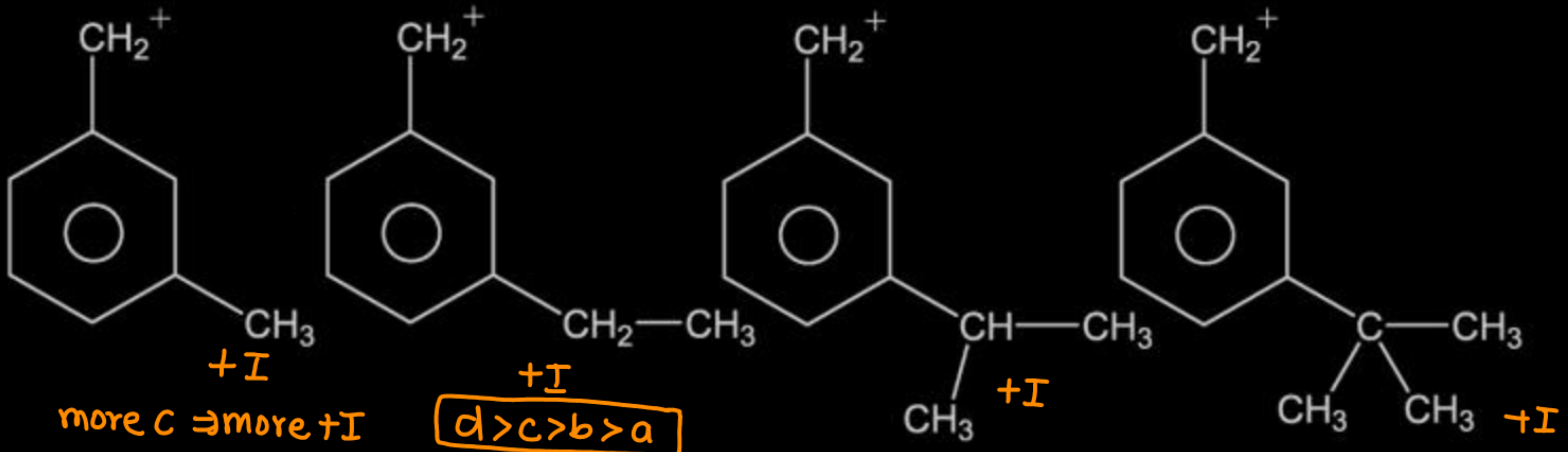


Q20.



a>b>c>d

Q21.

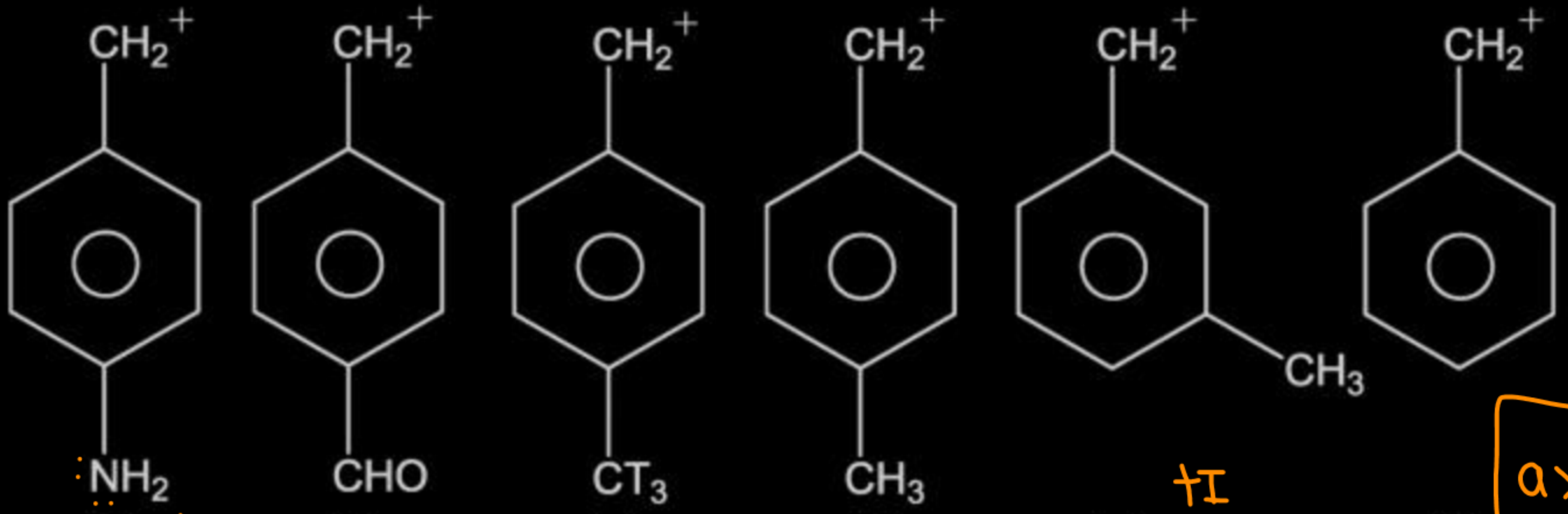


more C ⇒ more +I

d > c > b > a

PYQ

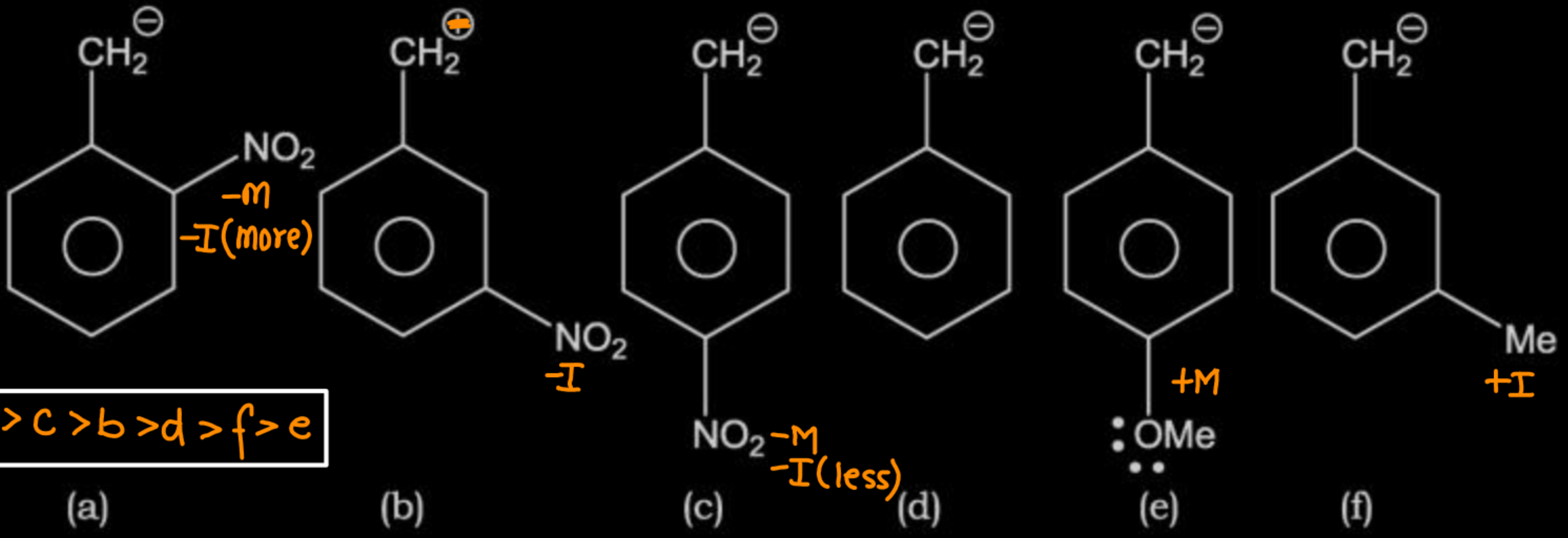
Q22.



(a) +M (b) −M (c) 3αT (d) 3αH (e) +I (f)

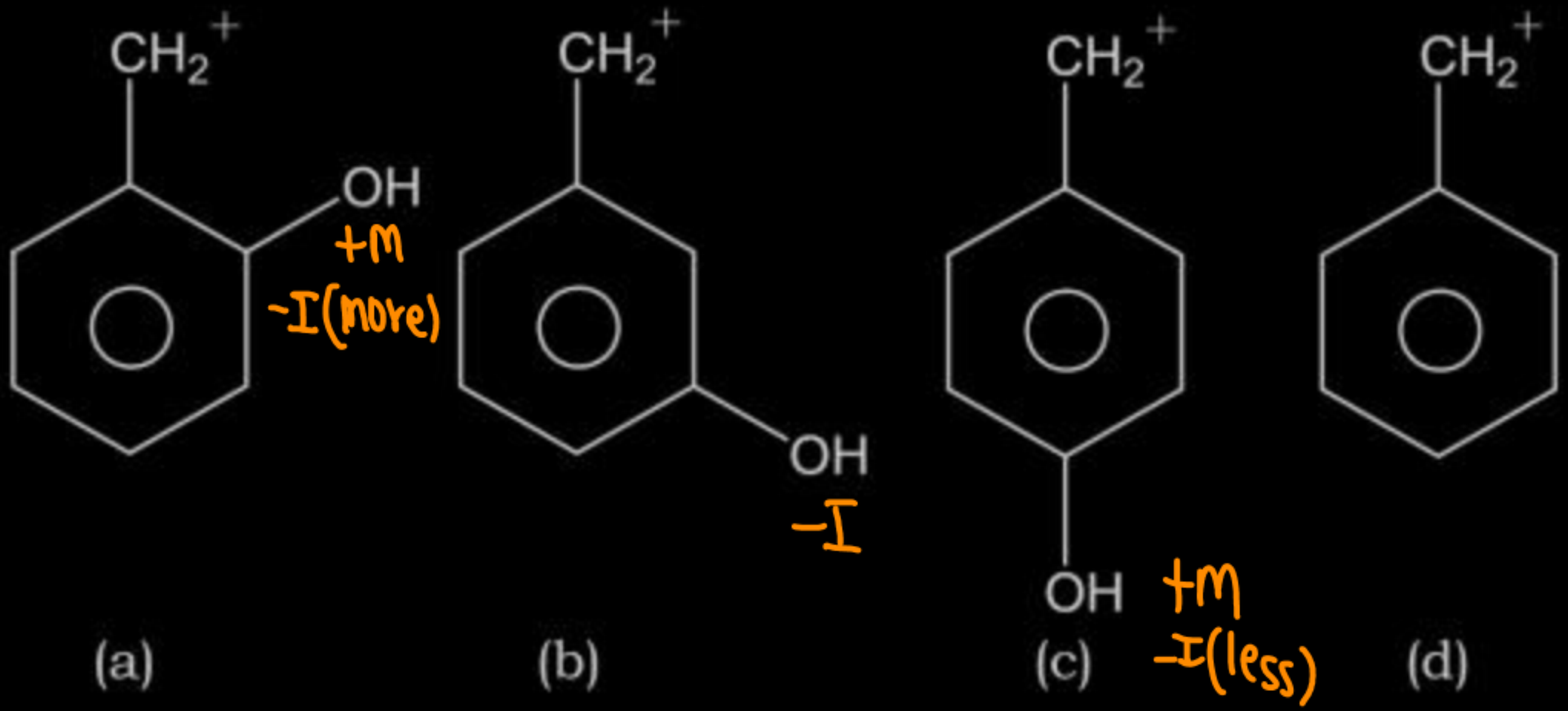
a > d > c > e > f > b

Q23.



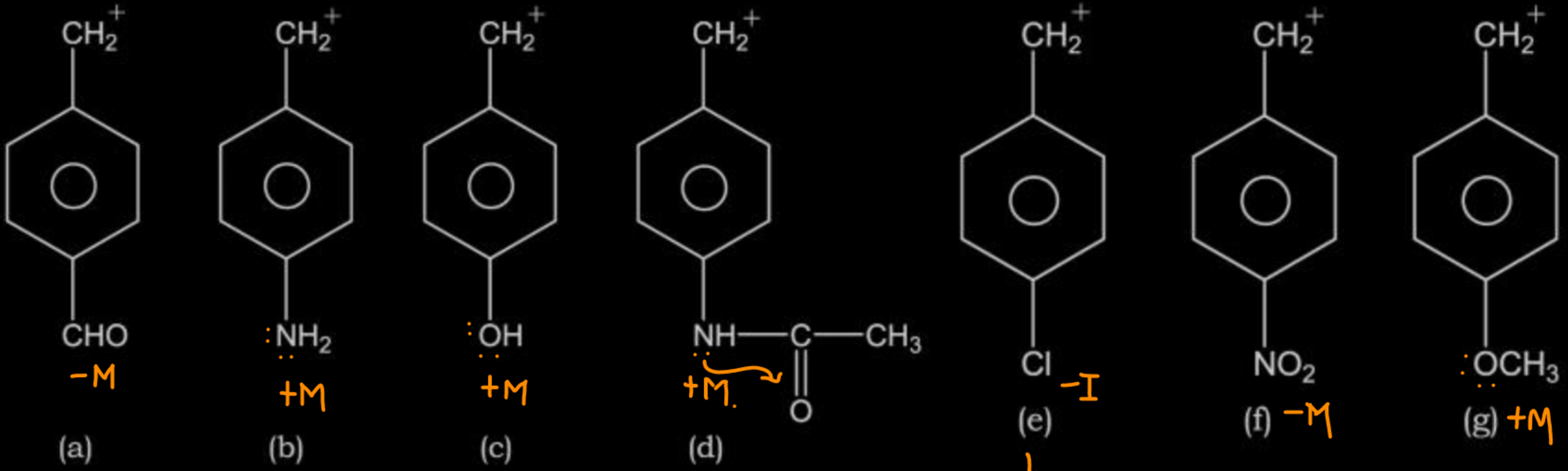
a > c > b > d > f > e

Q24.



c > a > d > b

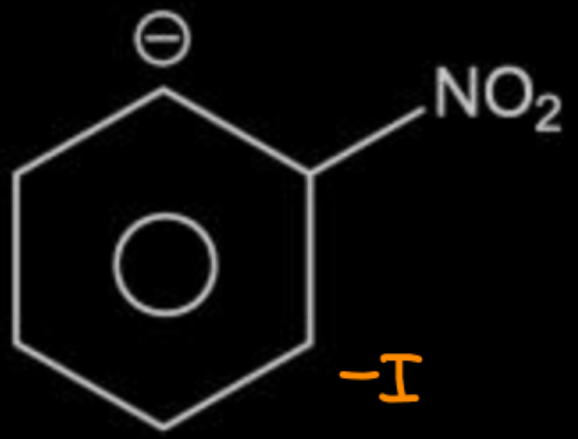
Q25.



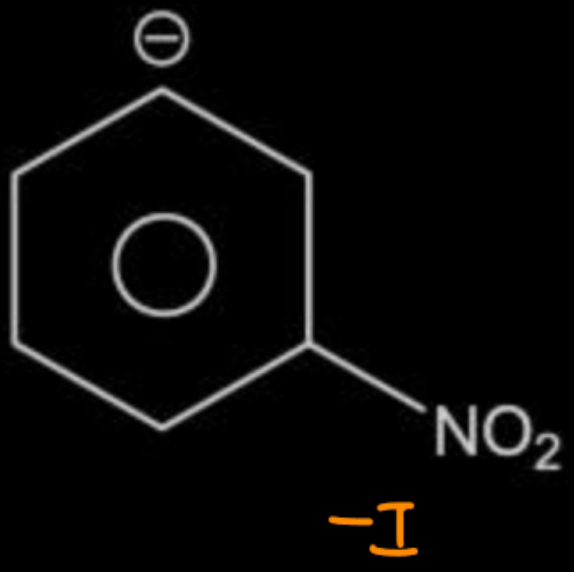
b > c > g > d > e > a > f

for halogen always -I

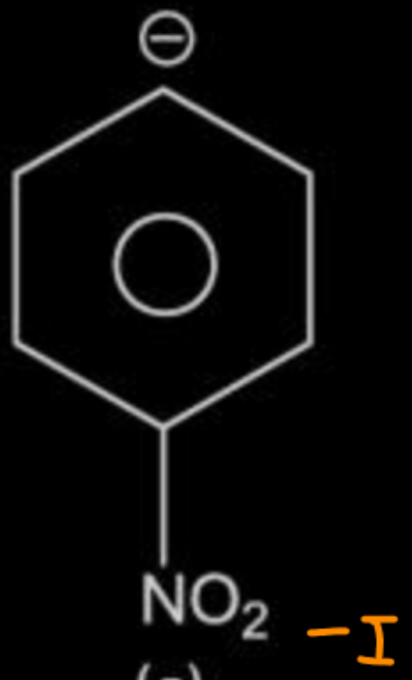
Q26.



(a)



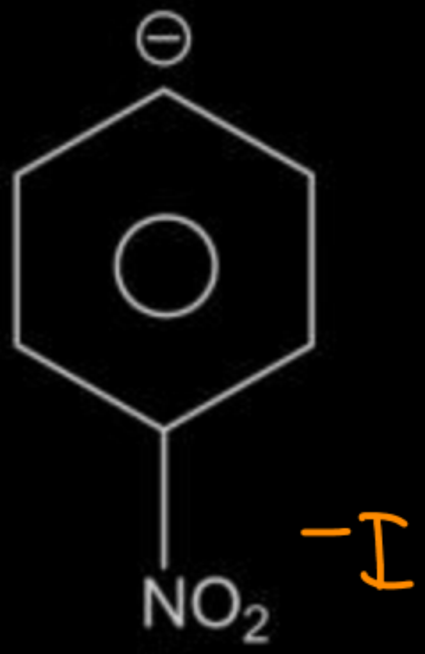
(b)



(c)

a > b > c

Q27.



(a)



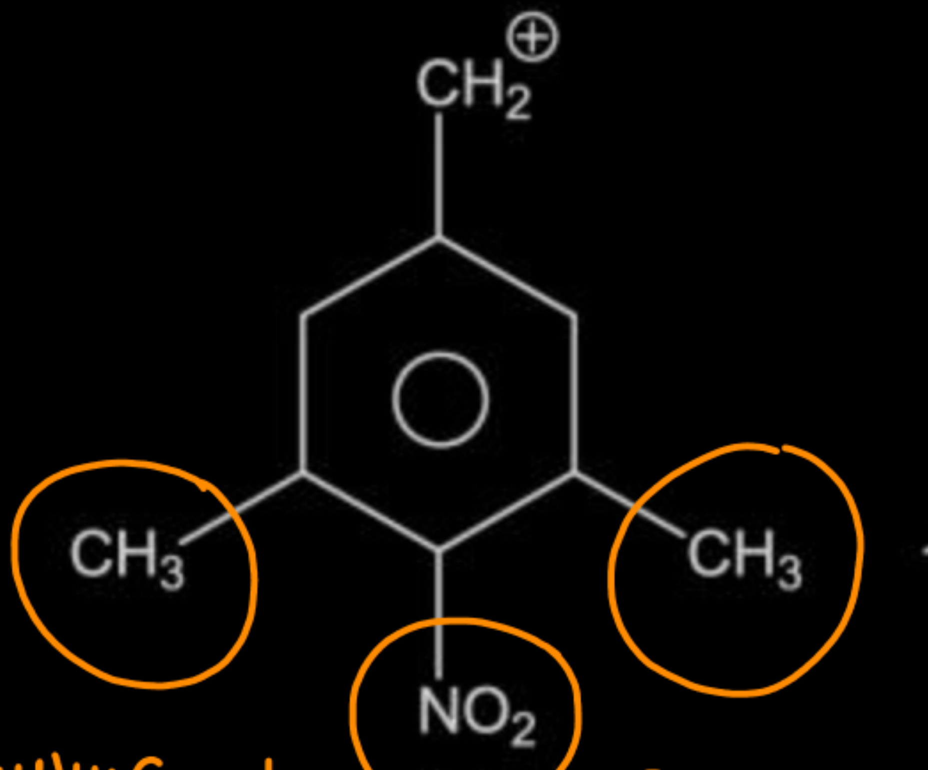
(b)

b > a

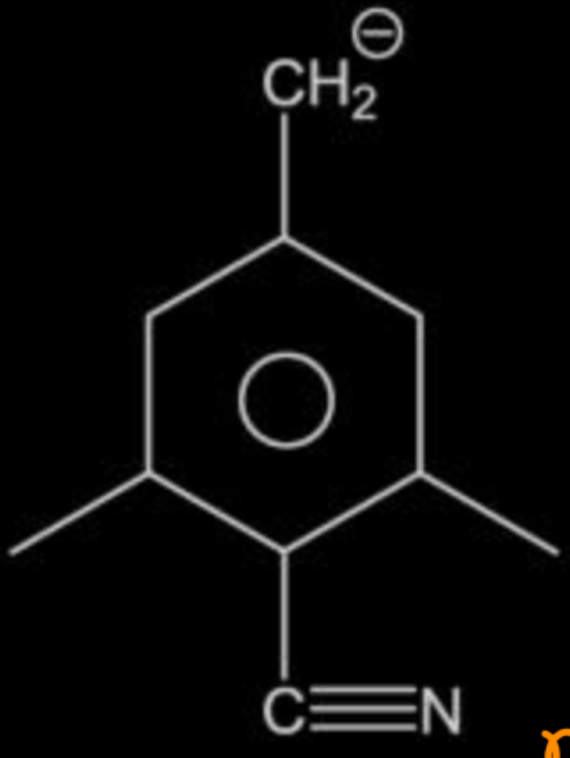
Small group → H/D/T/OH/NH_2/CN/F

Rest all are bulky group.

Q28.



(a)



(b)

Bulky Group
↳ Repulsion
↳ out of plane
↳ no Resonance

SIR effect

−I

−M

no SIR

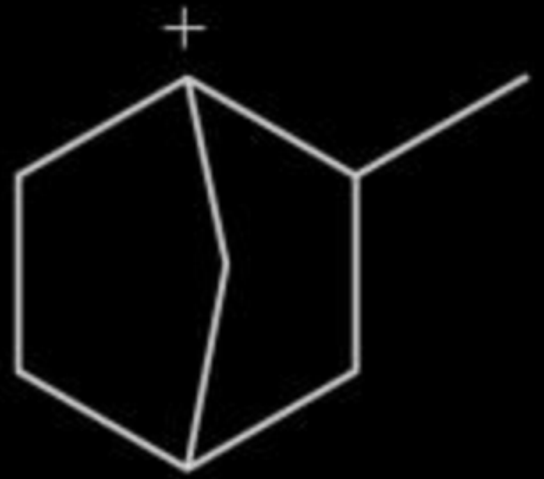
b > a

Q29. CH_3^+ (a) NH_4^+ (b)

b > a

Octet complete — Octet incomplete

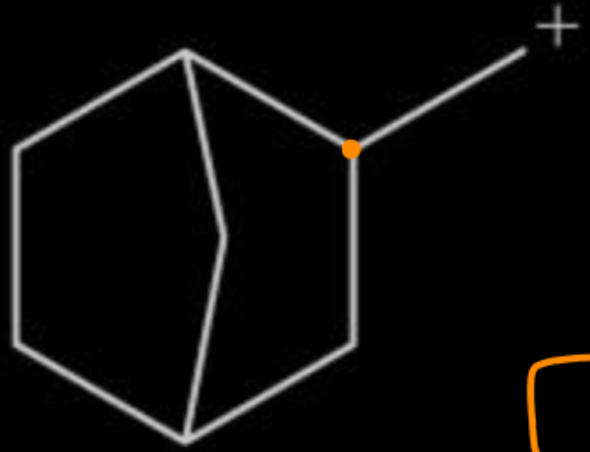
Q30.



(a) donotexist



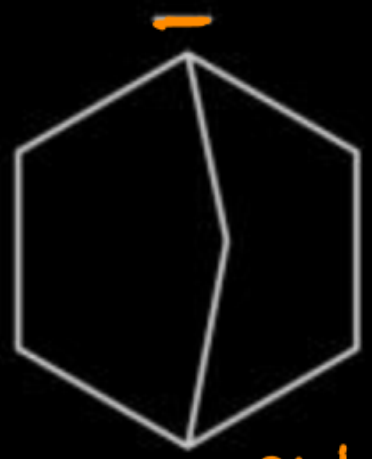
(b) 6α



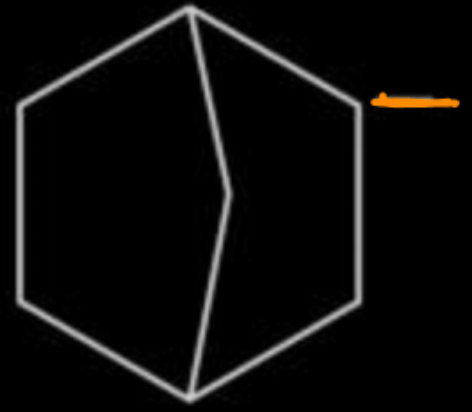
(c) 1α

b > c > a

Q31.



(a) exist
3° anion



(b) exist
2° anion

b > a

3° cation > 2° cation > 1° cation

Higher degree → Cation → Stable

Lower degree → anion → stable

1° anion > 2° anion > 3° anion

THANK YOU

Acidic & Basic Strength

① Acid → Comp which have tendency to donate H^+ is called acid.

② Acidic Strength ∝ Stability of Carbanion

③ $\propto -M \propto -I \propto \frac{1}{+I} \propto \frac{1}{+M}$

④ $\propto EWG \propto \frac{1}{EDG}$

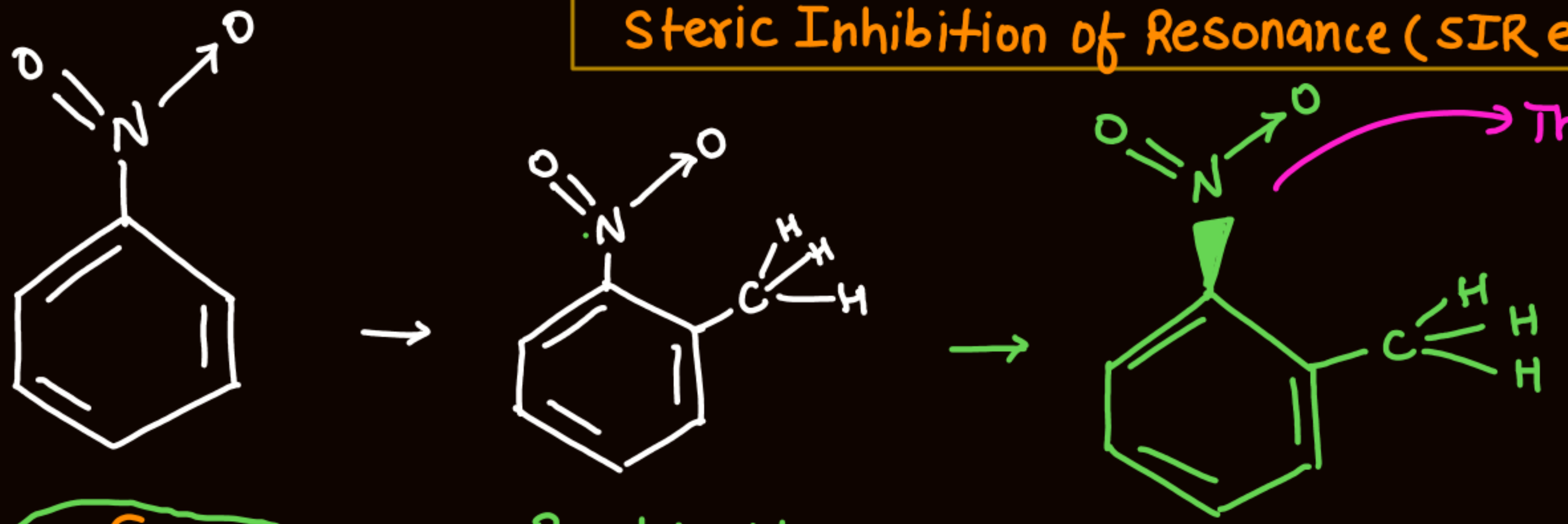
*** (याद) Acidic Strength $\propto K_a \propto \frac{1}{pK_a} \propto \frac{1}{K_b} \propto pK_b$

$$HCl \underset{H_2O}{\rightleftharpoons} H^+_{(aq)} + Cl^-_{(aq)}$$

$$\uparrow K_a = \frac{[H^+][Cl^-]}{[HCl]}$$

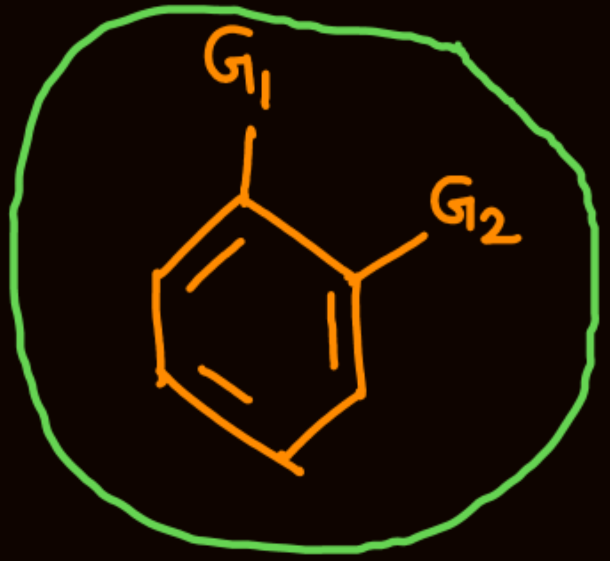
$$pK_a = -\log(K_a)$$

Steric Inhibition of Resonance (SIR effect)



Repulsion b/w Bulky Group

This group goes out of plane to avoid repulsion & this is k/a SIR.



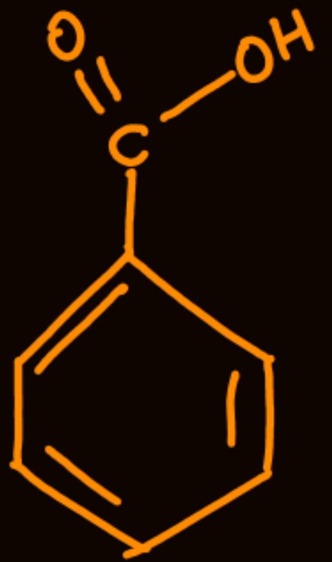
G_1 → Triangular Bulky Group $-NO_2$, $-\overset{O}{\overset{\|}{C}}-OH$, $-\overset{O}{\overset{\|}{C}}-OR$, $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-Cl$, $-\overset{O}{\overset{\|}{C}}-NH_2$ etc

G_2 → Bulky Group → $-R$, $-Cl$, $-Br$, $-I$, $-NO_2$, $-\overset{O}{\overset{\|}{C}}-OR$, $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-Cl$, $-\overset{O}{\overset{\|}{C}}-NH_2$ ...

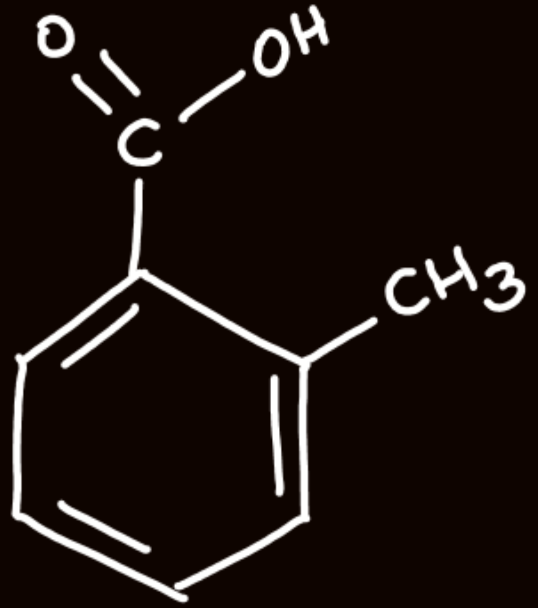
SIR → due to ortho Substitution of Bulky Group, G_1 feels Steric repulsion & due to this G_1 goes out of plane & Resonance stops. This is k/a SIR effect.

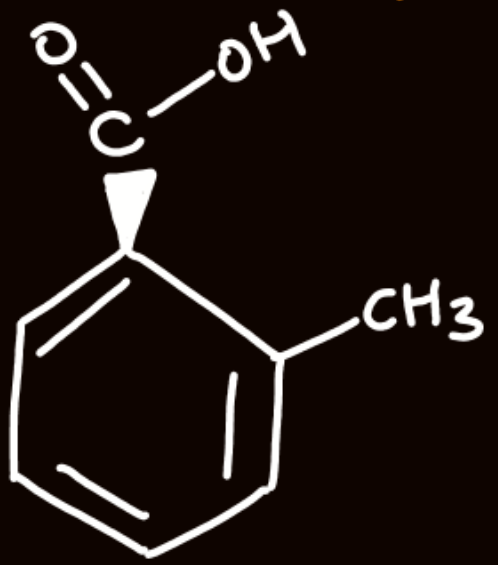
G_1 & G_2 Can never be Bulky Group → H | D | T | F | Cl | OH | NH_2 | $\bar{C}H_2$ | $\overset{+}{C}H_2$ | CN etc

Ortho-Effect → Benzoic acid & its derivative.
(due to SIR)

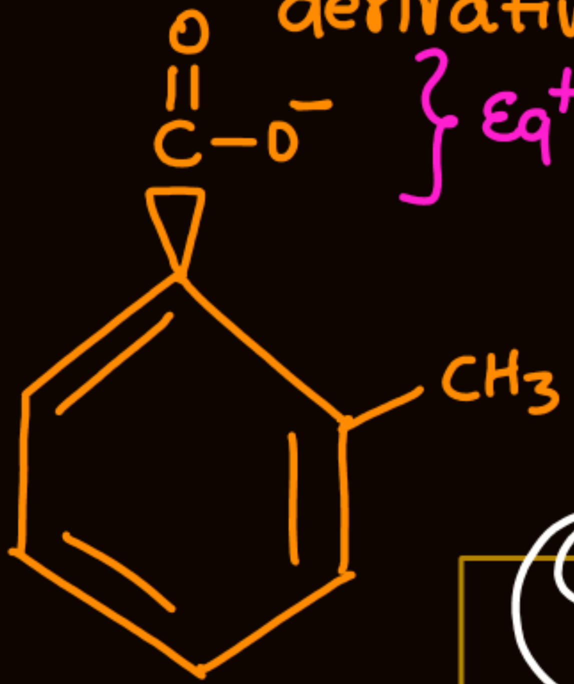


↓
normal Resonance
↓
less stability





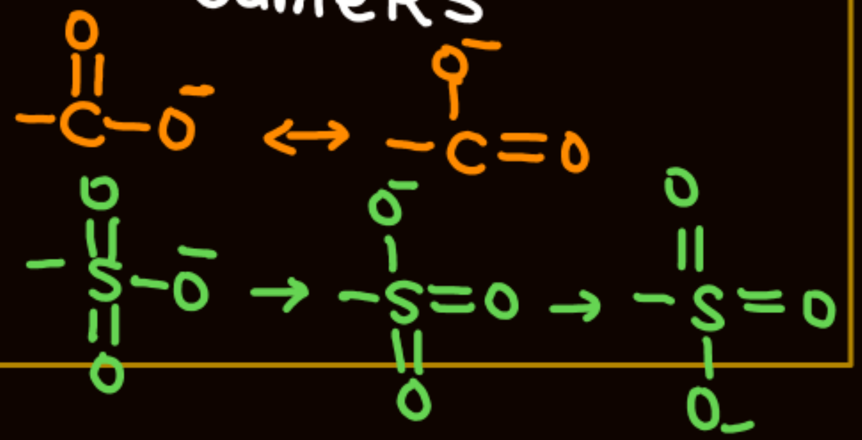
due to Repulsion Resonance of -COOH stops.



} Eq+ Resonance

↓
Repulsion
↓
Eq+ Reso
↓
more Stability
↓
more acidic

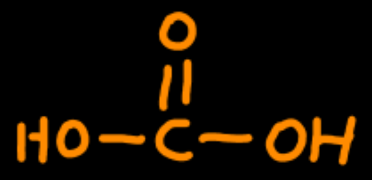
Eq+ Resonance
- equally contributing Resonance
- Same RS



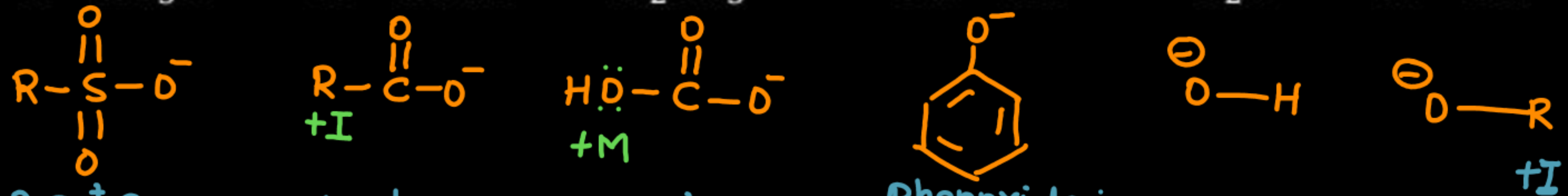
⇓
Eq+ Reso is far more stable than normal Resonance.

ortho effect → Ortho Substituted Benzoic acid is more acidic than its derivative (meta/para)

Question Compare acidic strength-



	Sulphonic acid	Carboxylic acid	Carbonic acid	Phenol / Carbolic acid	water	Alcohol
1.	$R-SO_3H$	$R-COOH$	H_2CO_3	$Ph-OH$	H_2O	$R-OH$



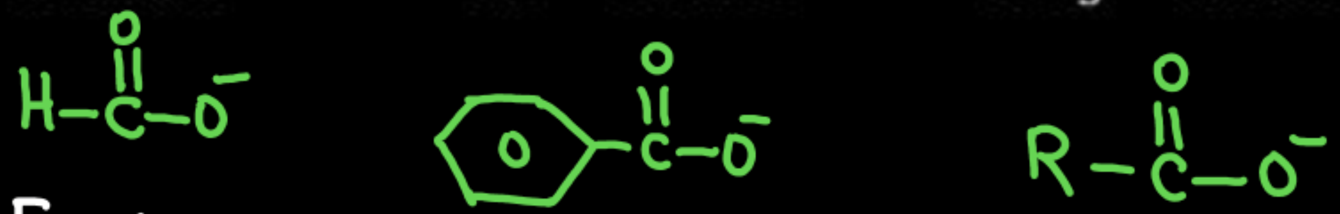
2 Eq^t Reso | 1 Eq^t Reso | 1 Eq^t Reso | Phenoxide ion normal Reso

1>2>3>4>5>6

H_2O is more acidic than R–OH.
except $CH_3-OH > H_2O$ (छोड़ु alcohol)

याद (ncert) (Exceptional)

2. $HCOOH$ | $Ph-COOH$ | CH_3-COOH



Formic acid | Benzoic acid | Acetic acid

HCOOH > PhCOOH > RCOOH
हमारा प्यारा Ramlal
acid पीता है

3. $HCOOH > CH_3COOH$ but $H-COOH < CH_2-COOH$ (with EWG on CH_2)

अगर Ramlal के पास EWG है then acidic str ↑
↓
–M | –H | –I

याद (Remember)

ncert → Pg-380

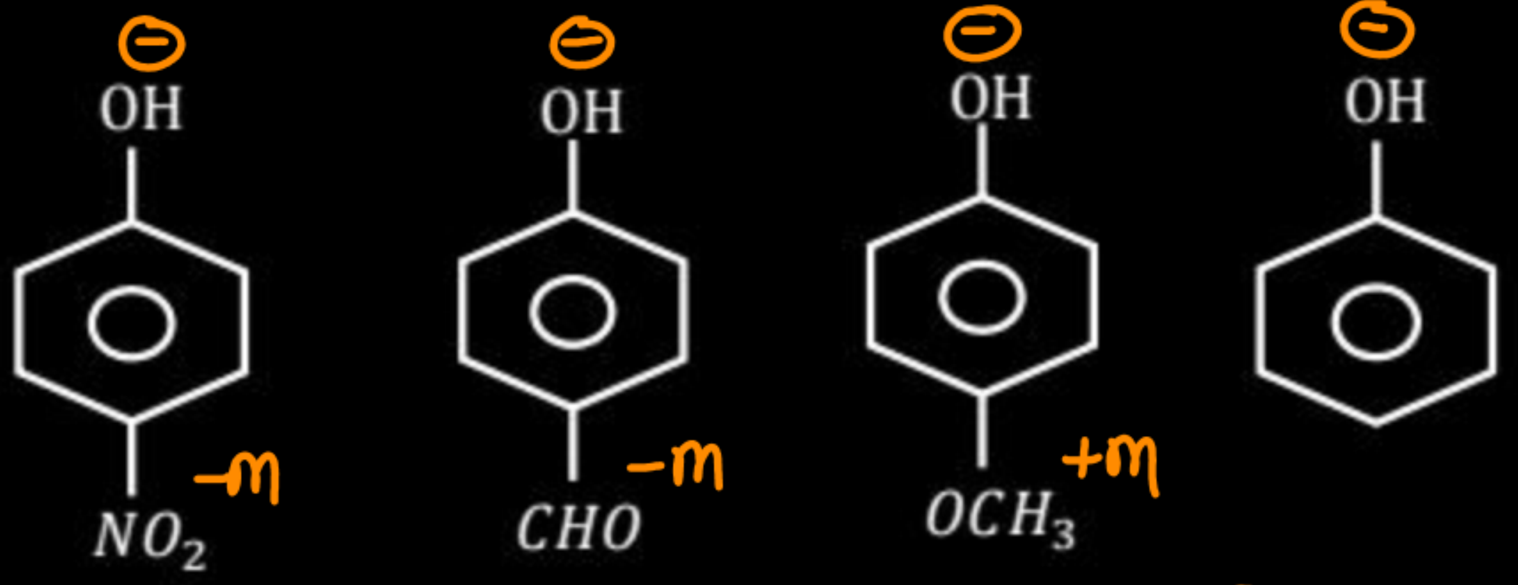
4. $CF_3-COOH > CCl_3-COOH > CHCl_2-COOH > CH_2(NO_2)-COOH >$

$CH_2(CN)COOH > CH_2(F)-COOH > CH_2(Cl)-COOH > CH_2(Br)-COOH > H-COOH >$

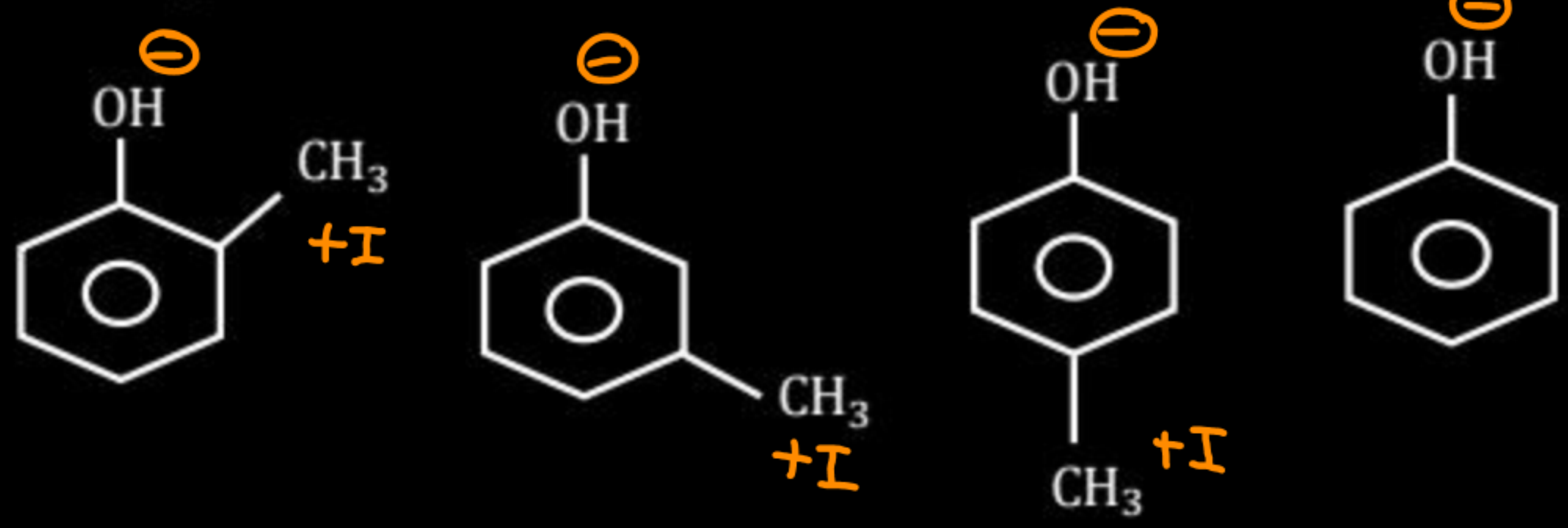
Formic acid

$CH(Cl)-CH_2-COOH > Ph-COOH > CH_2(Ph)-COOH > CH_3-COOH > CH_3-CH_2-COOH$

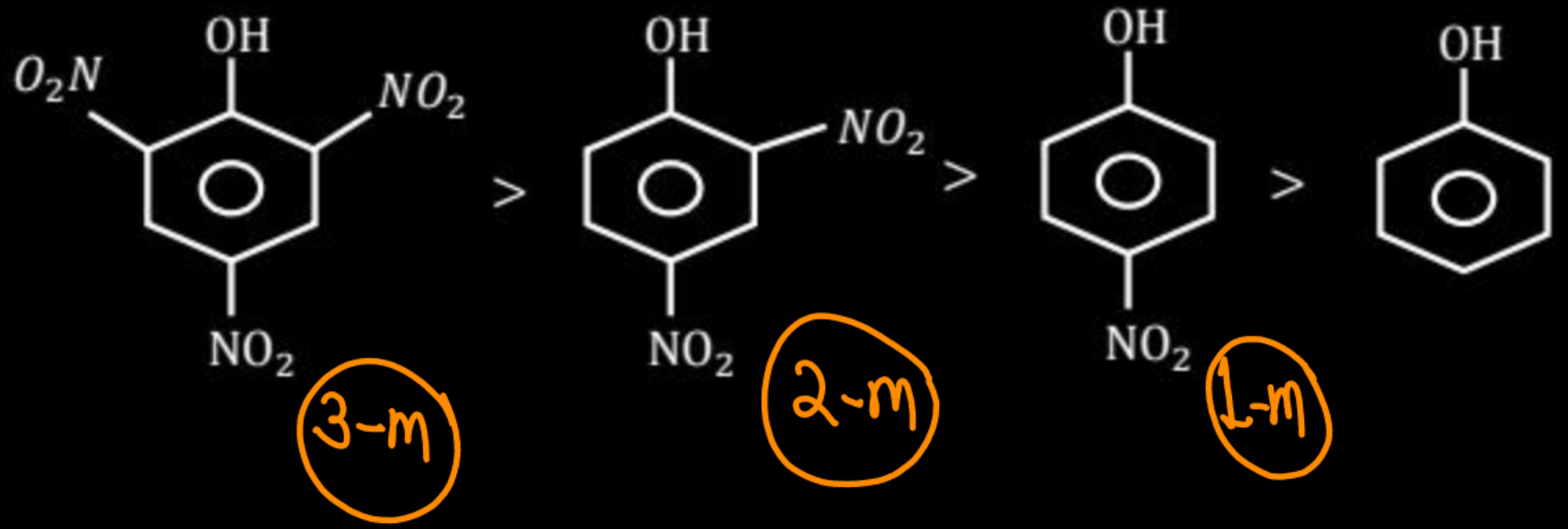
(Based on pKa Value)



a > b > d > c

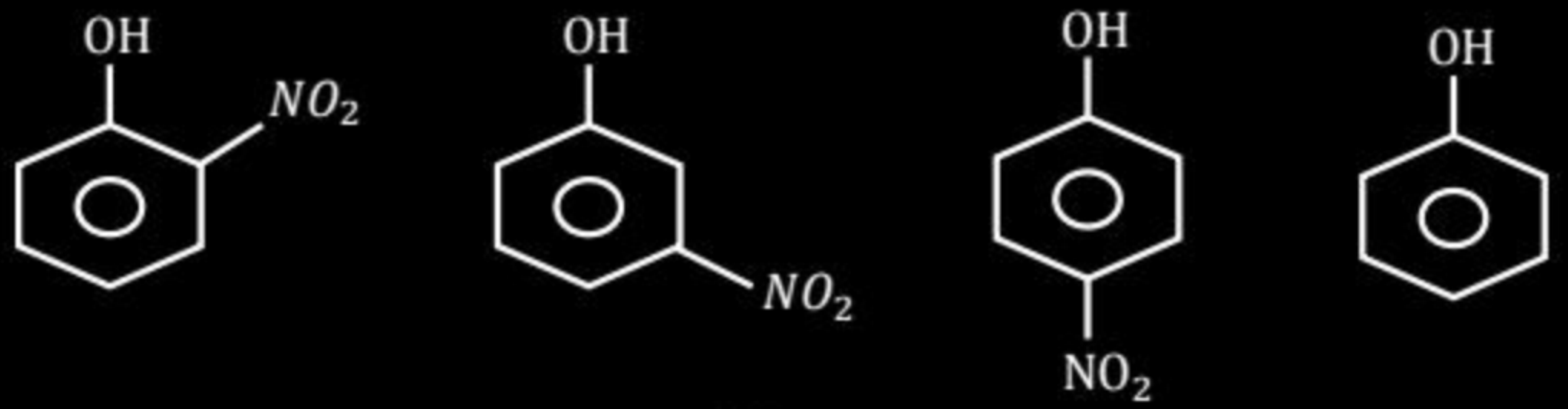


d > c > b > a



a > b > c > d

याद



disintefactant.

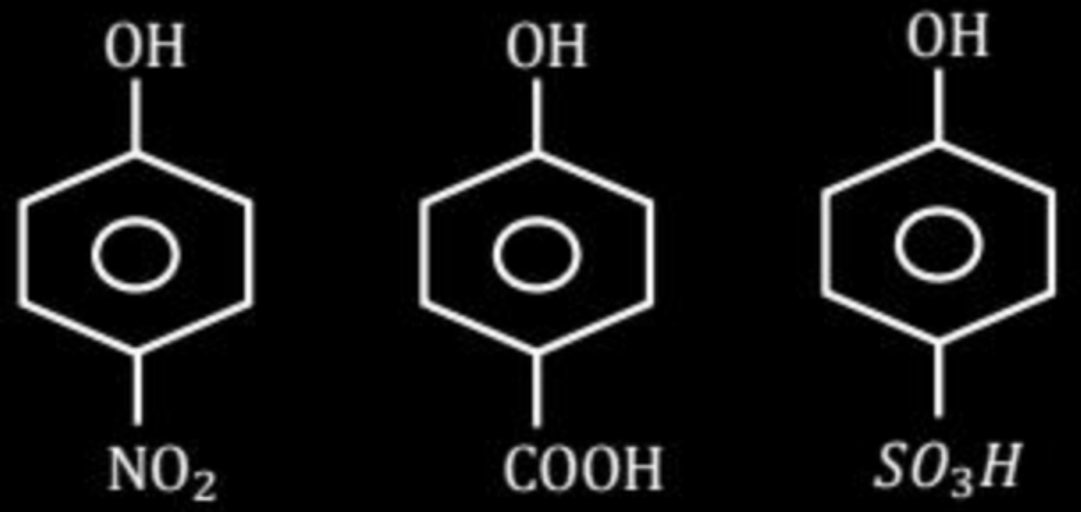
↑

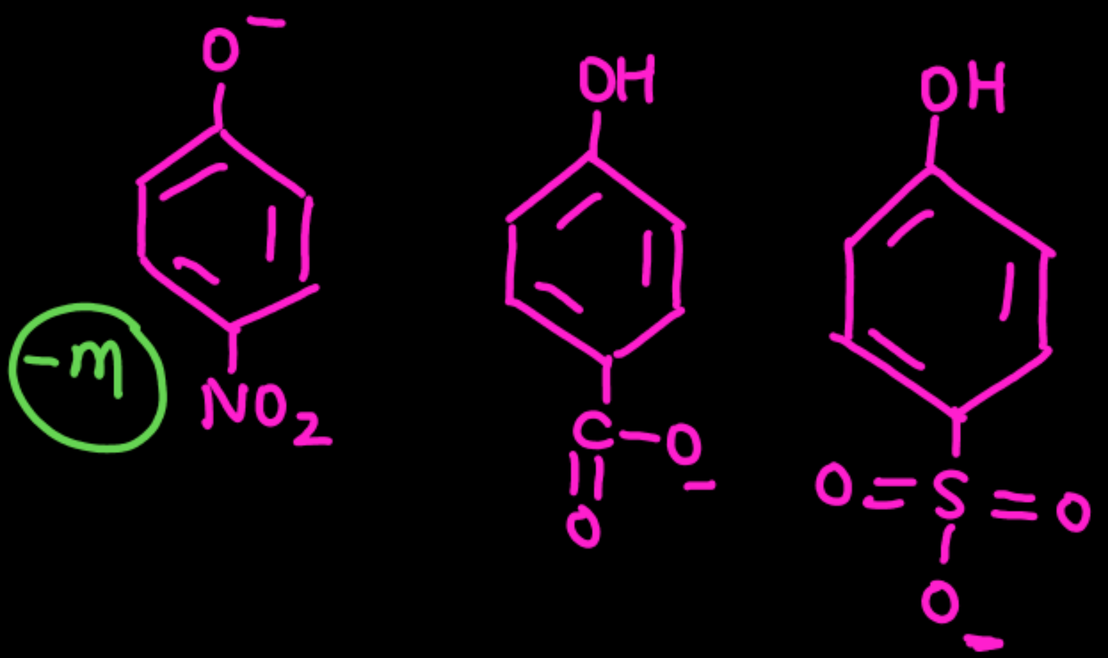
पियो मत phenol

P > O > M > phenol

c > a > b > d

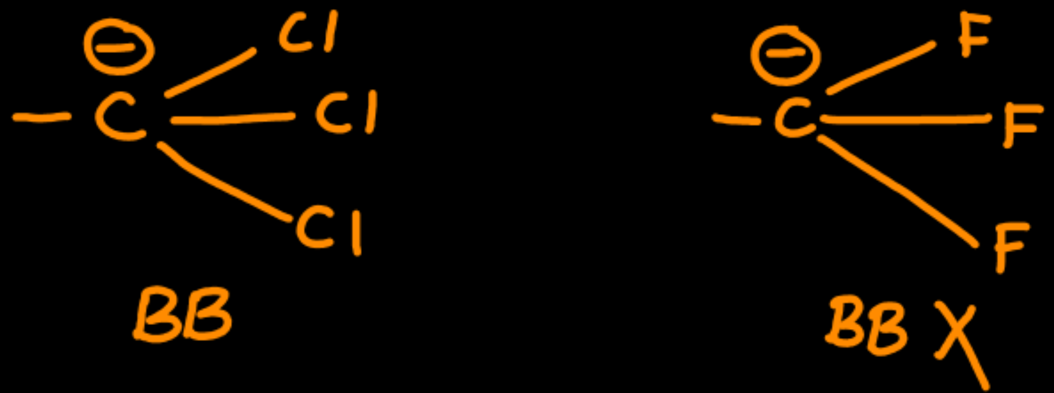
Q



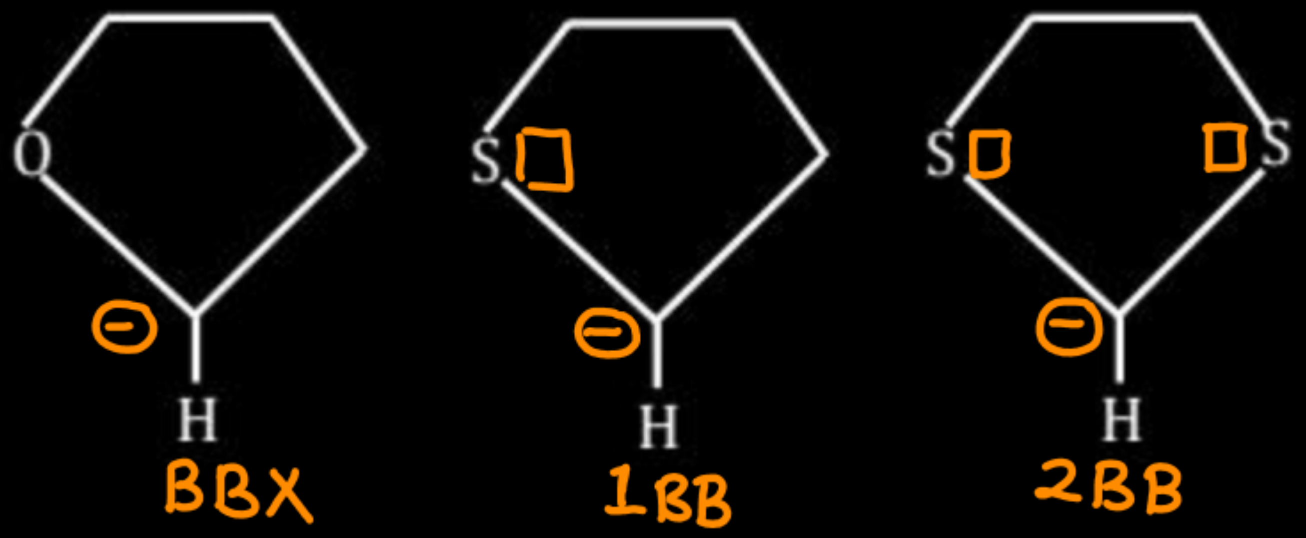


3 > 2 > 1

10. $-CHCl_3$ > $-CHF_3$



11.



c > b > a

12.

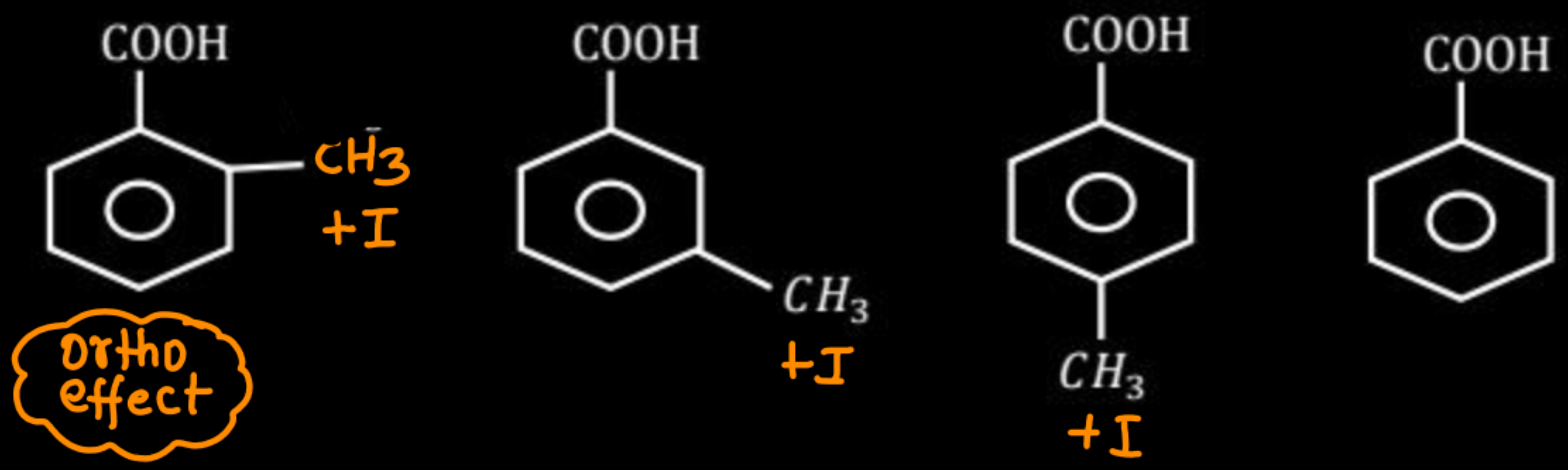


CH ≡ CH

sp carbon

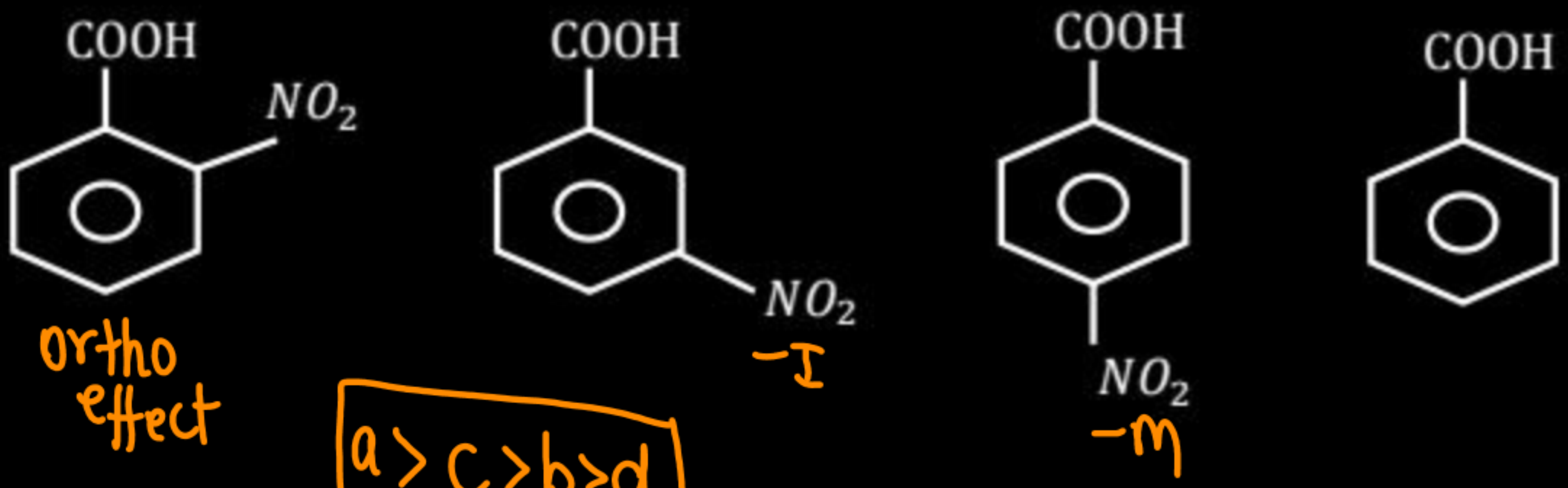
a > b

13.

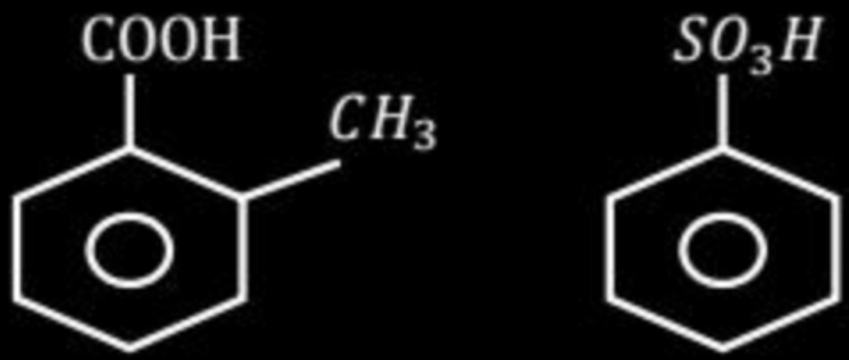


a > d > c > b

14.



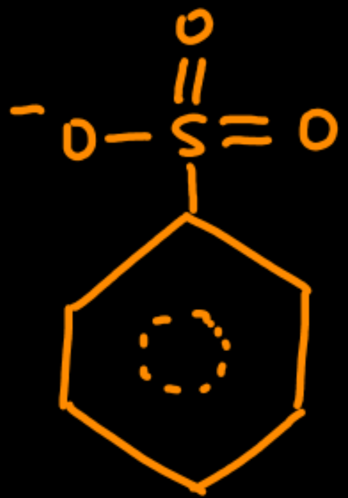
a > c > b > d

15. 

SIR

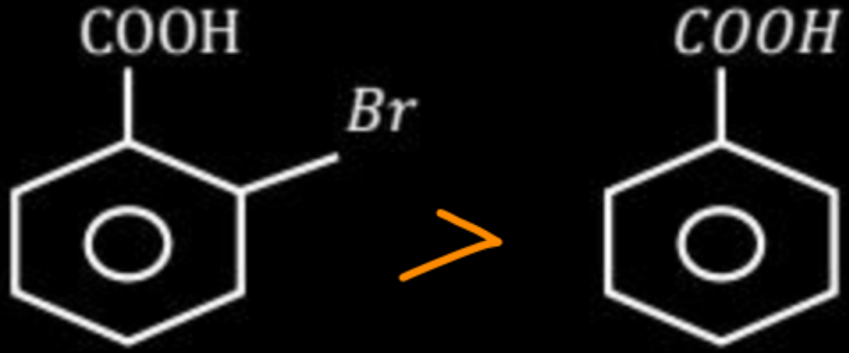


Eq⁺ Reso

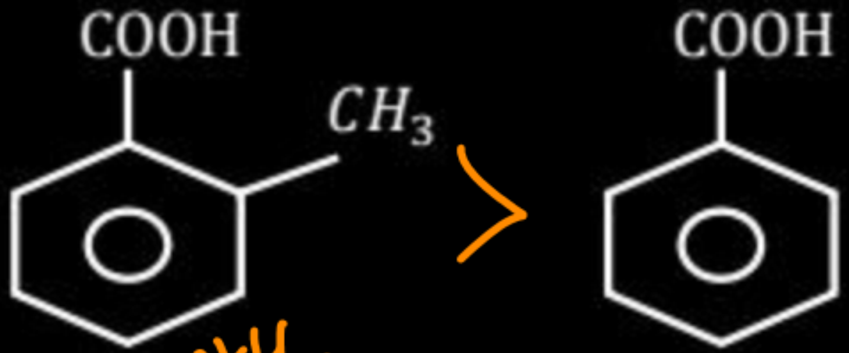


normal Reso

1>2

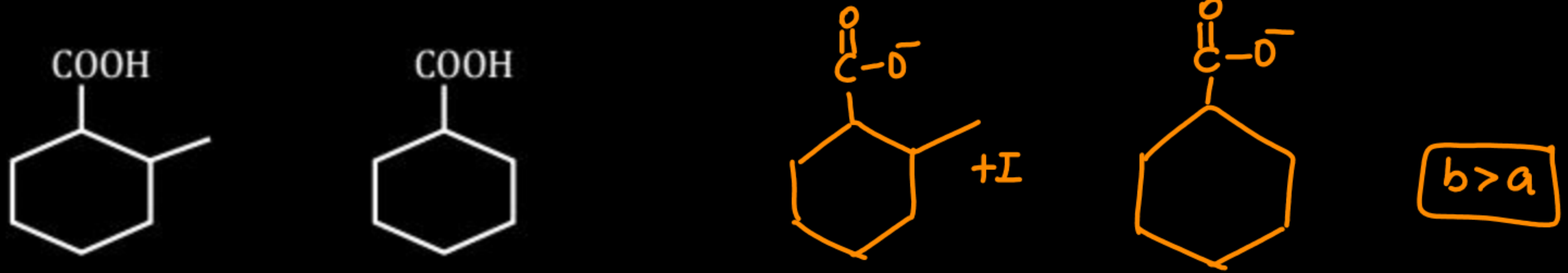
16. 

ortho effect

17. 

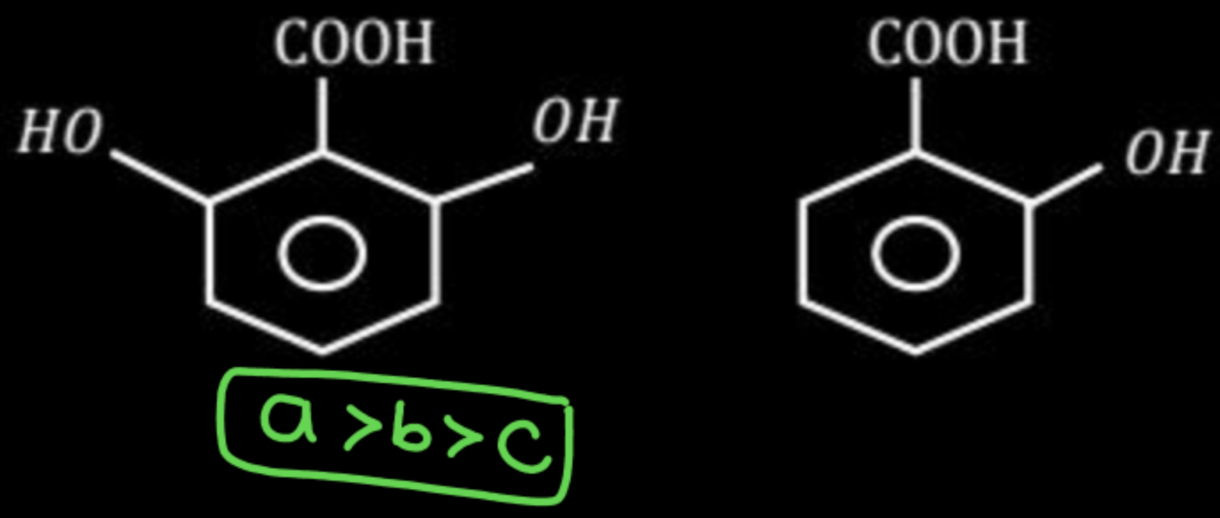
ortho effet

18.

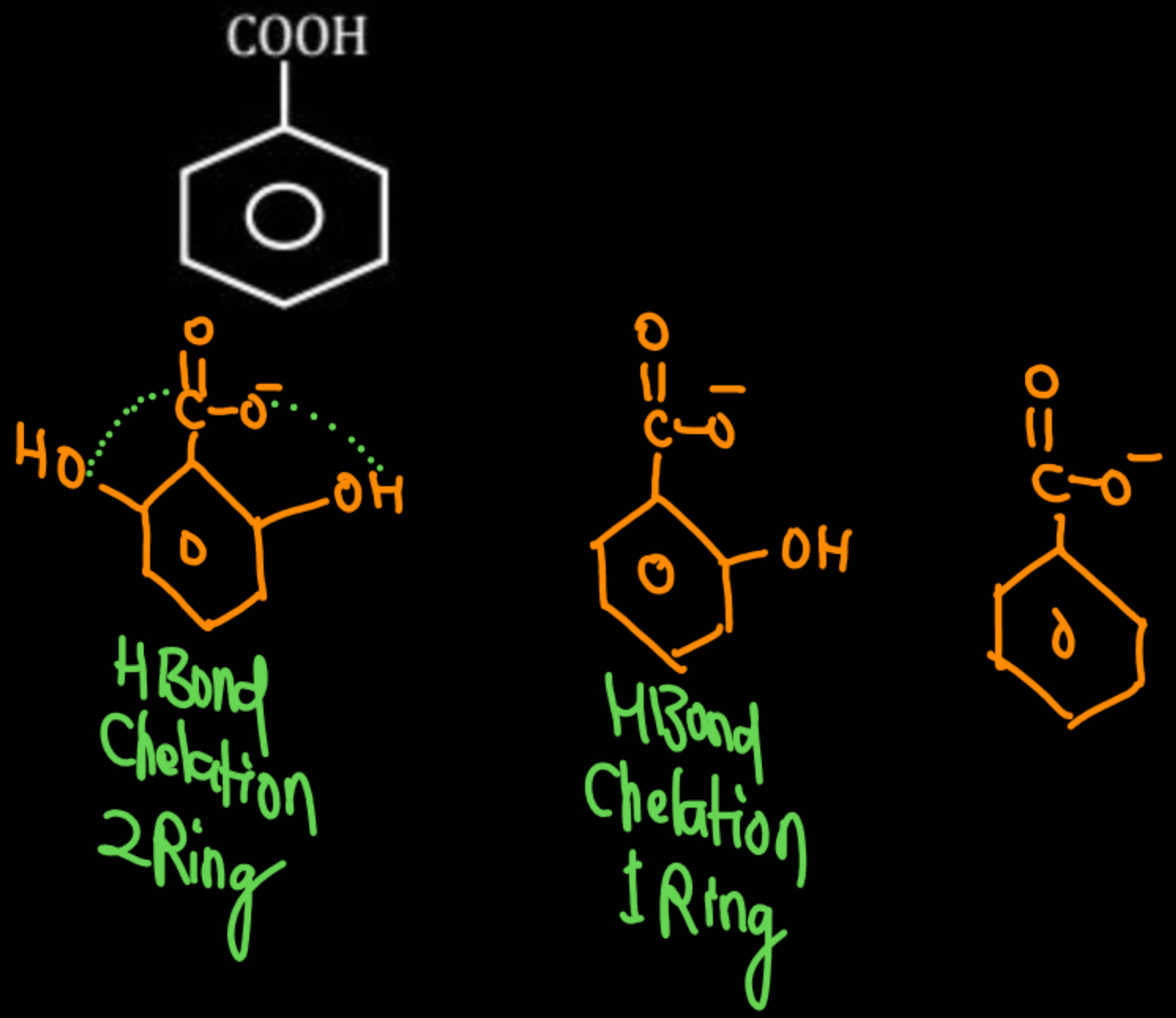


COOH
COOH
+I
b>a

19.

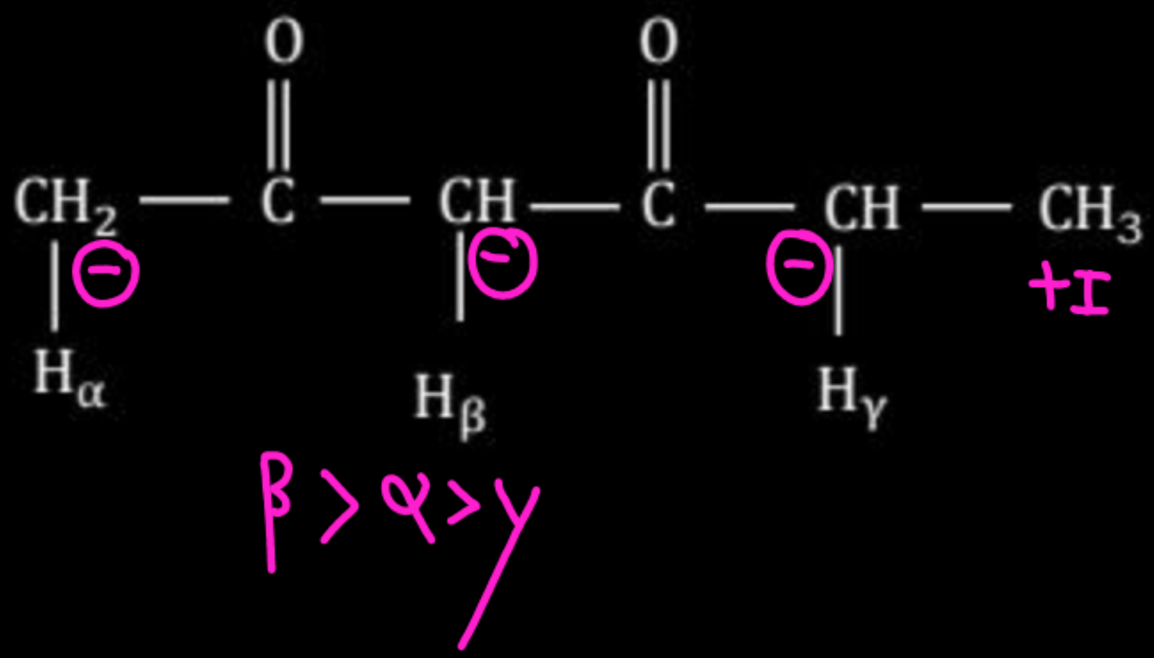


COOH
HO
OH
COOH
OH
a>b>c



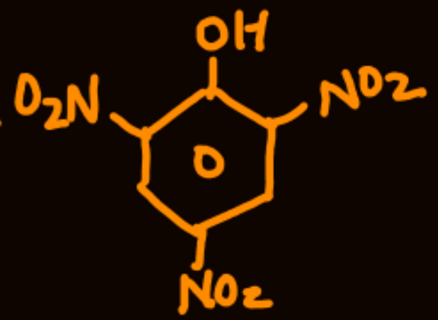
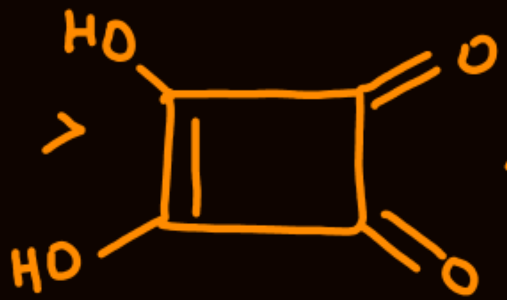
COOH
HO
OH
H Bond Chelation 2 Ring
OH
H Bond Chelation 1 Ring

20.



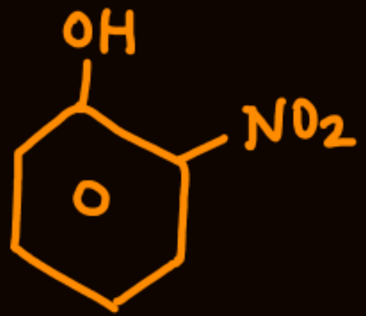
O
O
CH2
C
CH
C
CH
CH3
Hα
Hβ
Hγ
+I
β > α > γ

General acidic order

$R-SO_3H > H_3O^+ > CF_3-COOH >$  $>$  $> HCOOH > PhCOOH > RCOOH >$

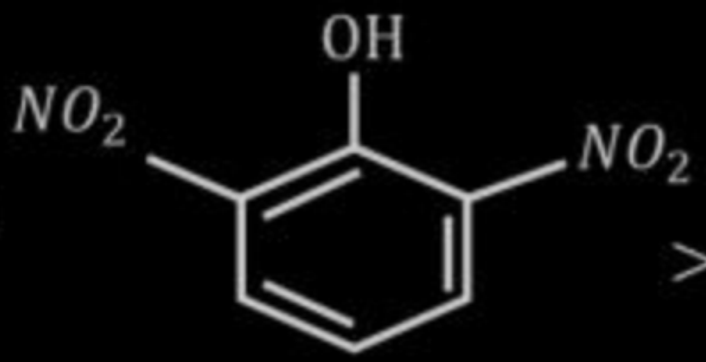
Picric acid

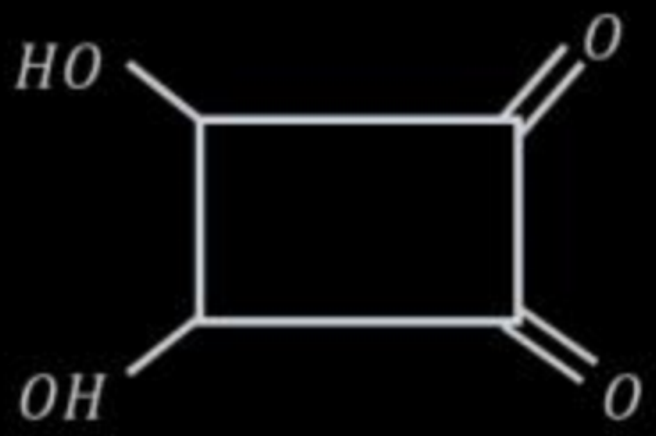
Squaric acid

$H_2CO_3 >$  $> HCN > \overset{+}{N}H_4 >$  $> H_2O > R-OH > CH \equiv CH > NH_3 > CH_2=CH_2$

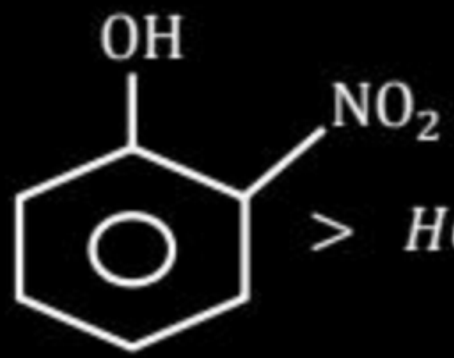
$> CH_3-CH_3$

Generic acidic order

$R - SO_3H > H_3O^+ > CF_3 - COOH >$ 

$>$ 

$> HCOOH >$

$Ph - COOH > R - COOH > H_2CO_3 >$ 

$> HCN > NH_4^+ >$ 

$>$

3.5 3.25 3.0 2.75 2.50

$H_2OH > R - OH > CH \equiv CH > NH_3 > CH_2 = CH_2 > CH_3 - CH_3$

Note - H_2O is more acidic than alcohol except $CH_3 - OH$ (alchol)

Basic Strength

→ Which can donate lonepair
→ Which can accept H^+.

$$\text{Basic Strength} \propto \text{Stab of Carbocation} \propto +M \propto +H \propto +I \propto \frac{1}{-M} \propto \frac{1}{-H} \propto \frac{1}{-I}$$

$$\propto \text{tendency to donate lonepair}$$

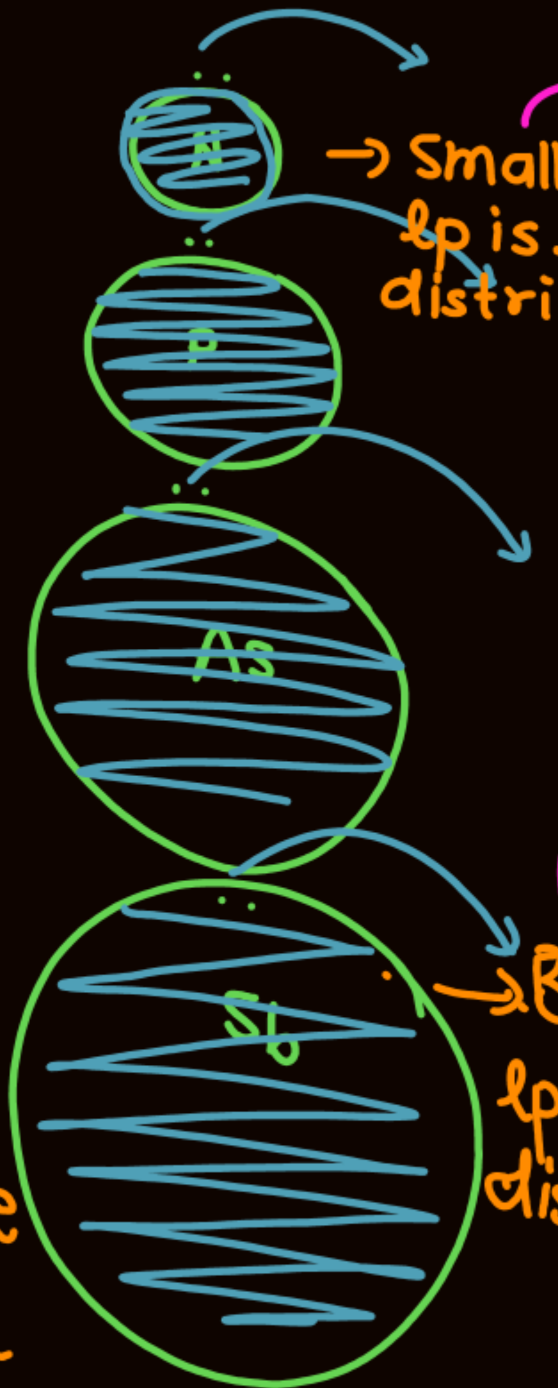
$$\propto \frac{1}{EN} \propto \frac{1}{\text{size}}$$

* याद *

$$\text{Basic Strength} \propto K_b \propto \frac{1}{pK_b} \propto \frac{1}{K_a} \propto pK_a$$

* For same group elements → −Ve charge Lonepair on Bigger Size → Stable ↓ less donate ↓ less basic

* For same period elements → −Ve charge lonepair On more En atom − stable ↓ less donate ↓ less basic

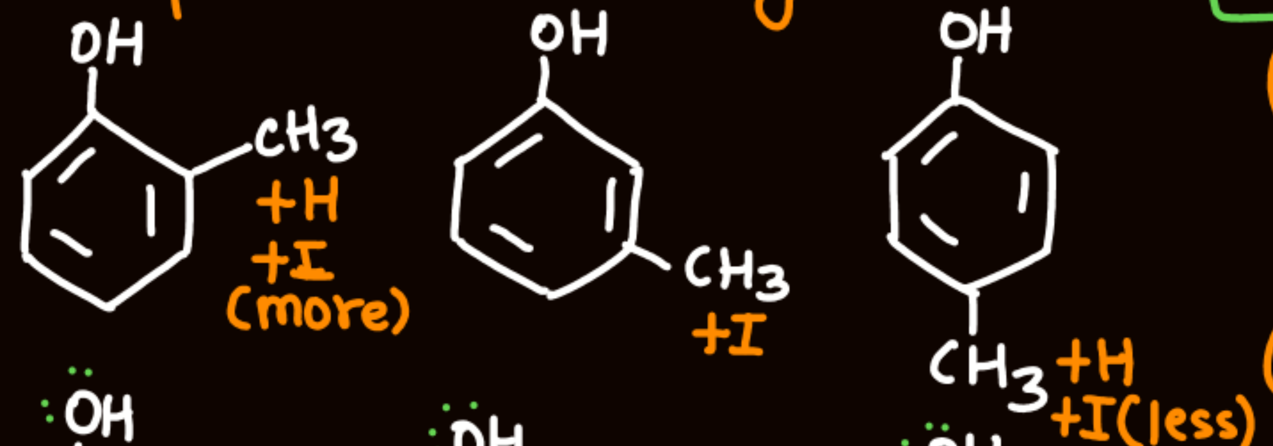


→ Small size, lp is less distributed → donate more

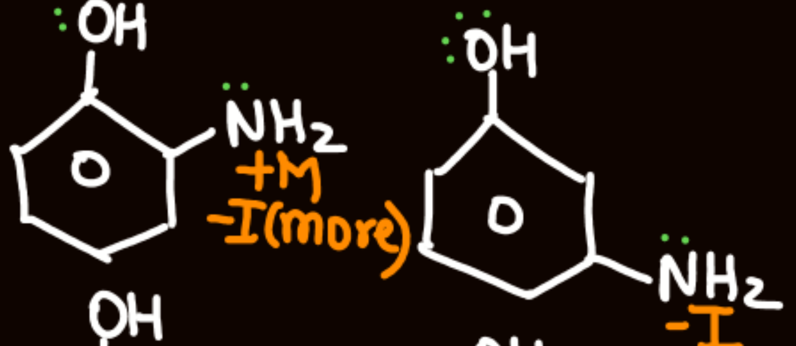
→ Big size, lp is more distributed → donate less

Que Compare Basic Strength —

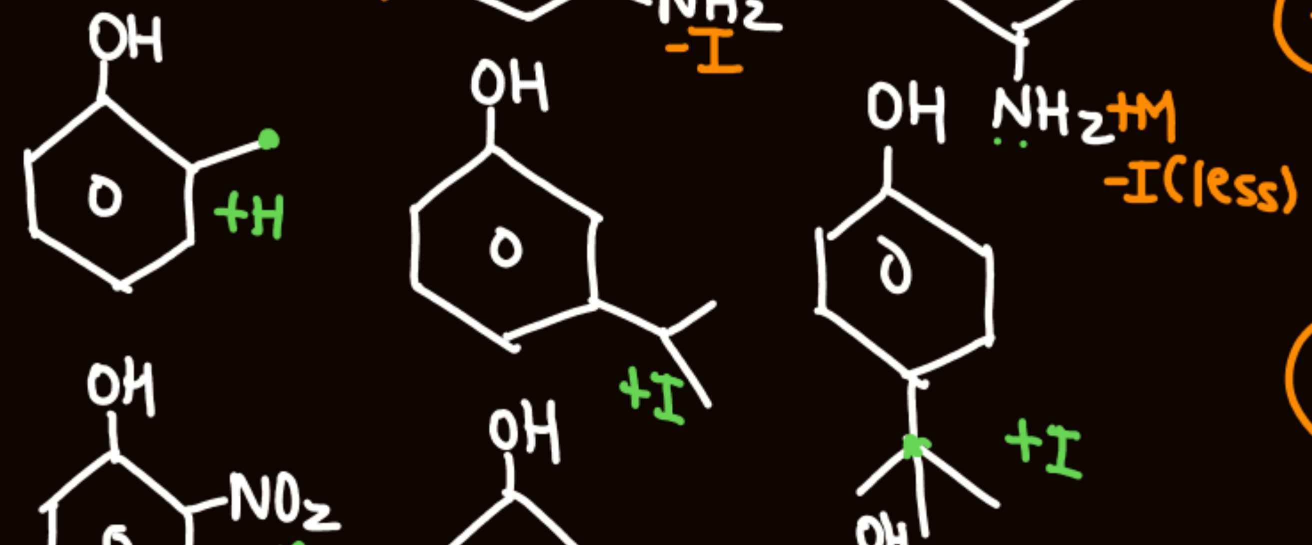
① **a>c>b**



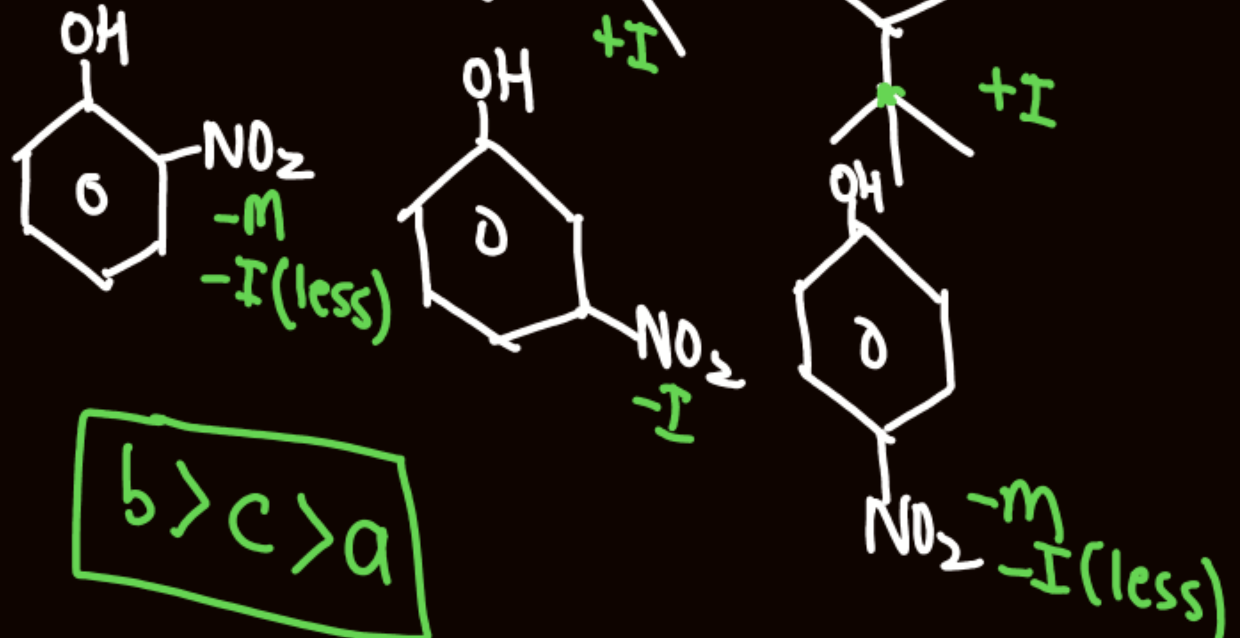
② **c>a>b**



③ **a>b>c**

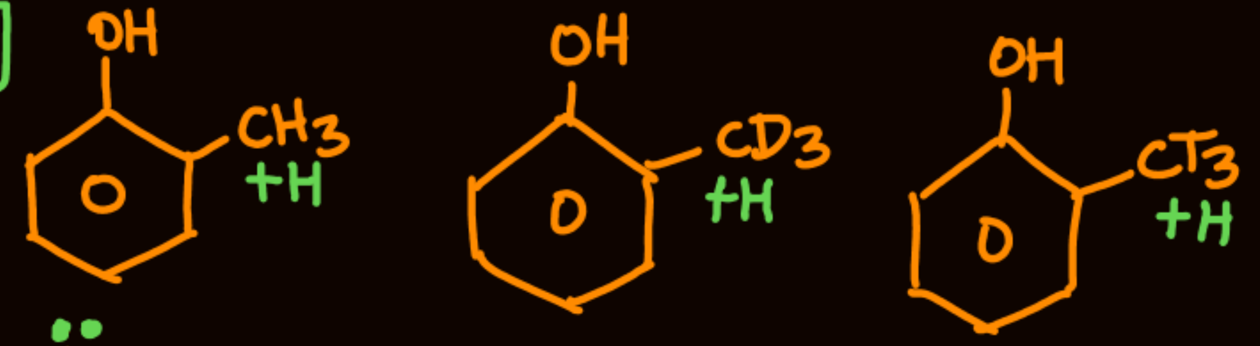


④

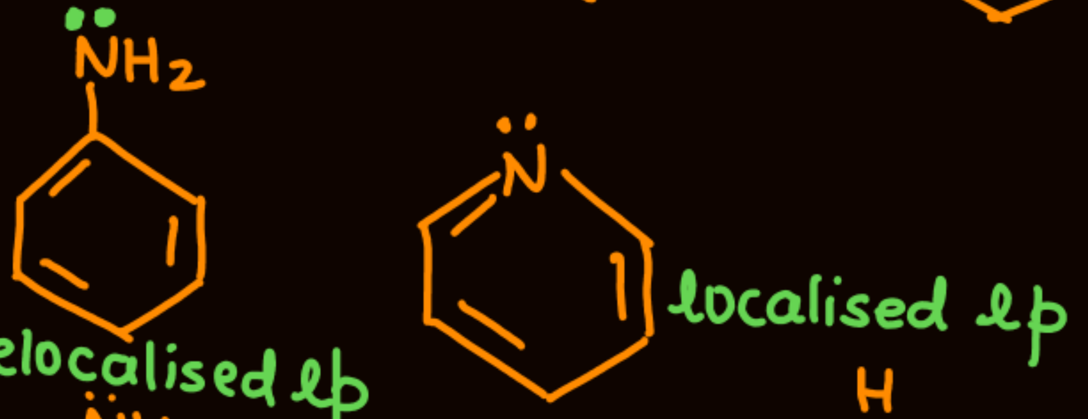


b>c>a

⑤ **a>b>c**

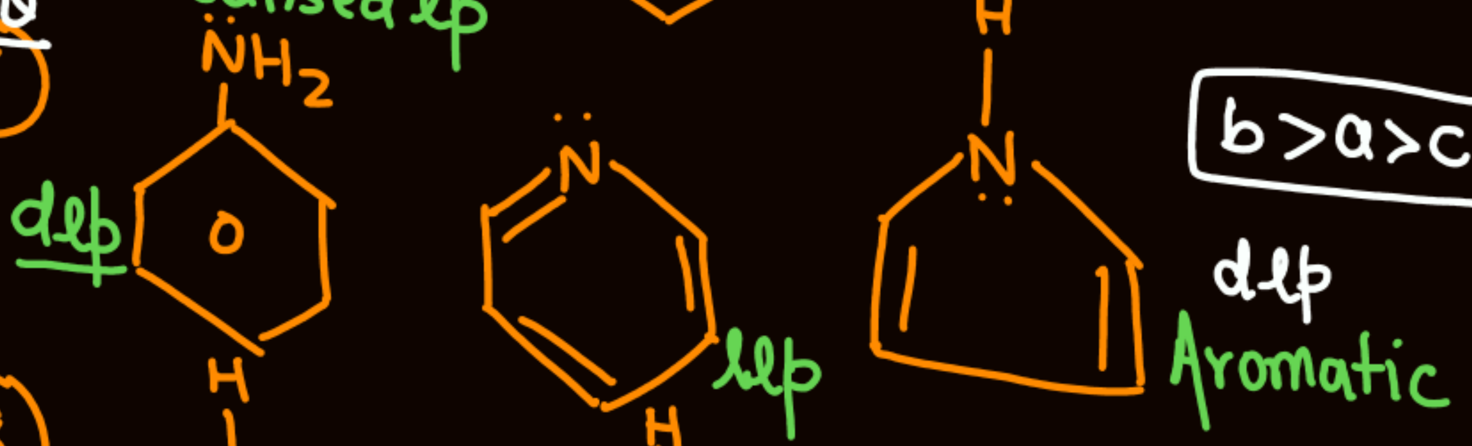


⑥ **b>a**

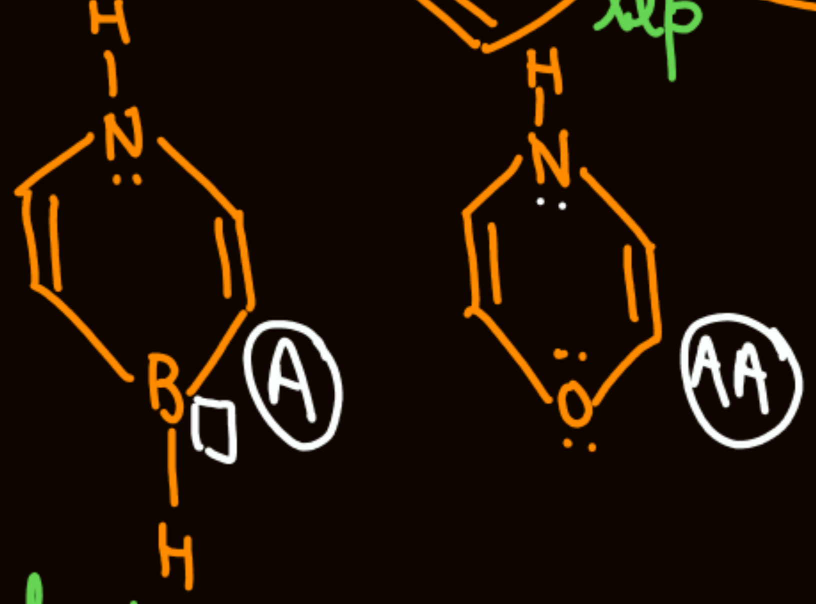


2016 Pyq

⑦ **b>a>c**

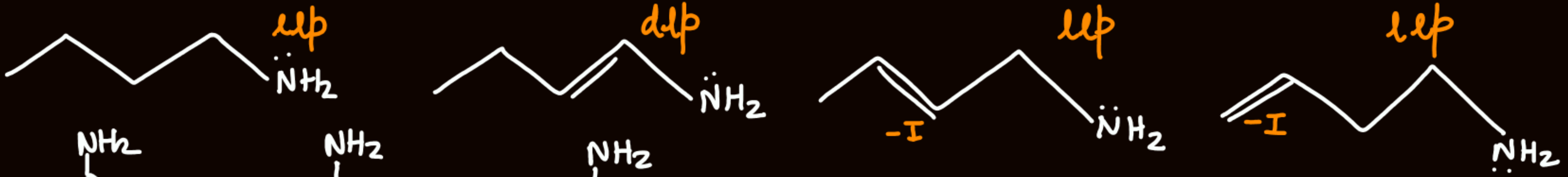


⑧ **b>a**



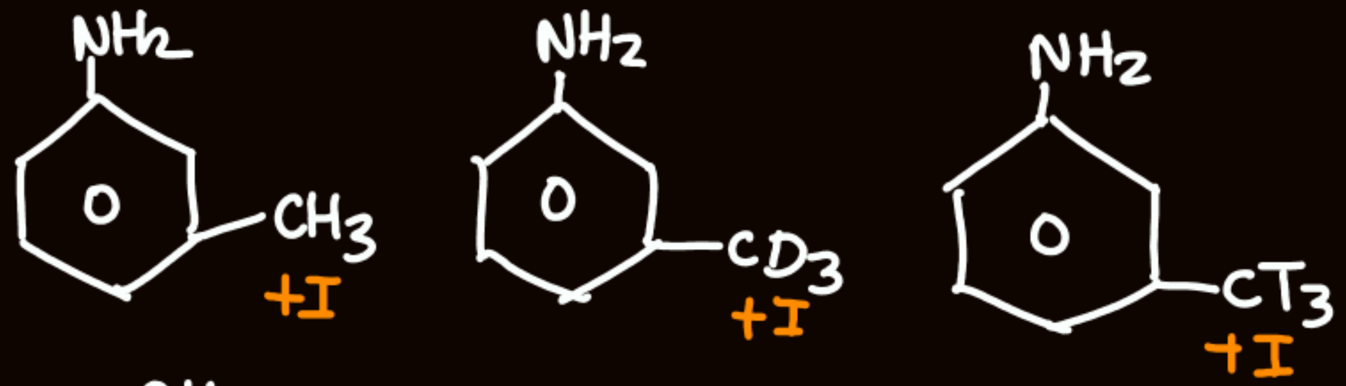
* localised lp has more basic strength always.

(9)



a > d > c > b

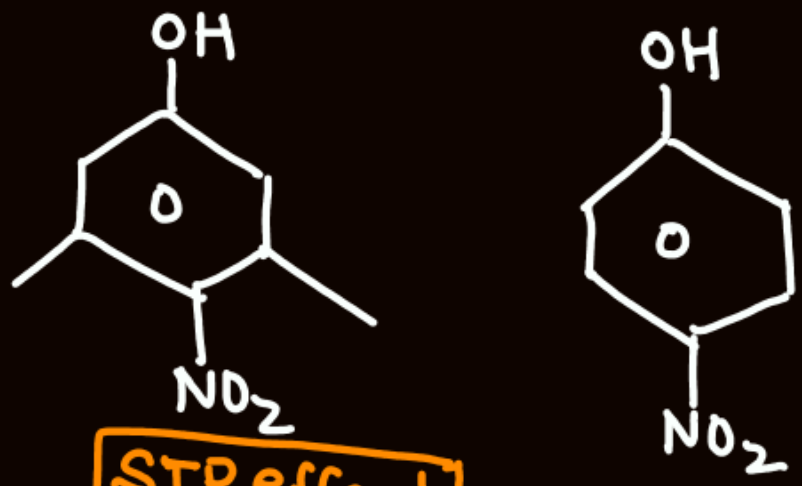
(10)



c > b > a

AIIMS

(11)



a > b

SIR effect

NO_2 → Reso → ✗

−M ✗

−I ✓

−M

Basic Strength in amine

Gaseous phase (always) → 3° amine > 2° amine > 1° amine

$$R-\ddot{N}(R)-R \;>\; R-\ddot{N}H(R) \;>\; R-\ddot{N}H_2$$

AQueous phase → 2° amine > 3° amine > 1° amine

R → Ethyl (231)

$$Et-\ddot{N}H(Et) \;>\; Et-\ddot{N}(Et)-Et \;>\; Et-\ddot{N}H_2$$

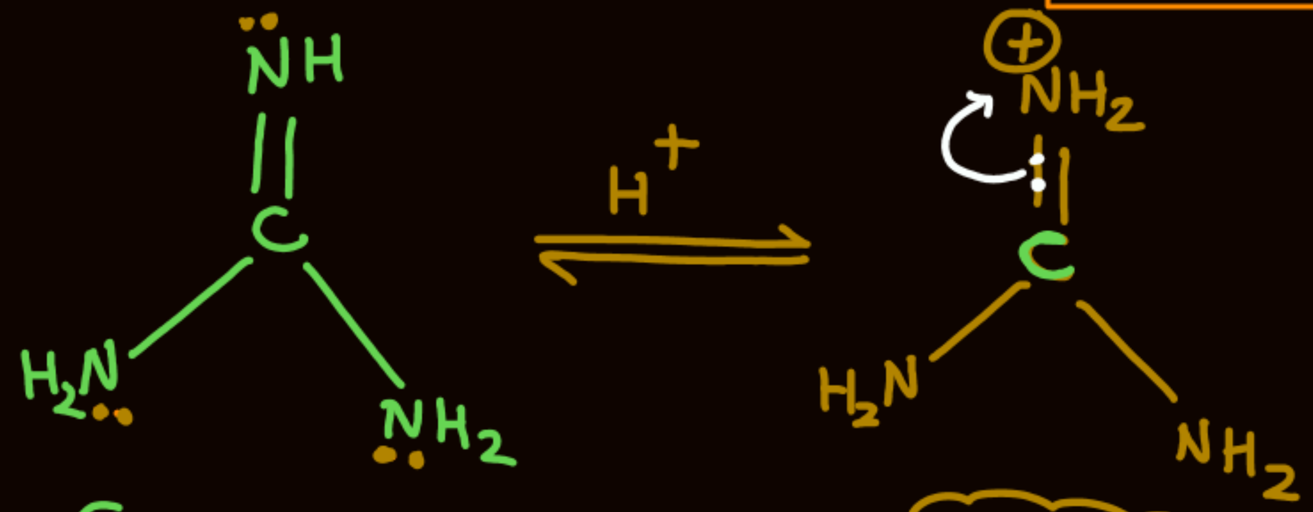
R → methyl (213) → 2° amine > 1° amine > 3° amine

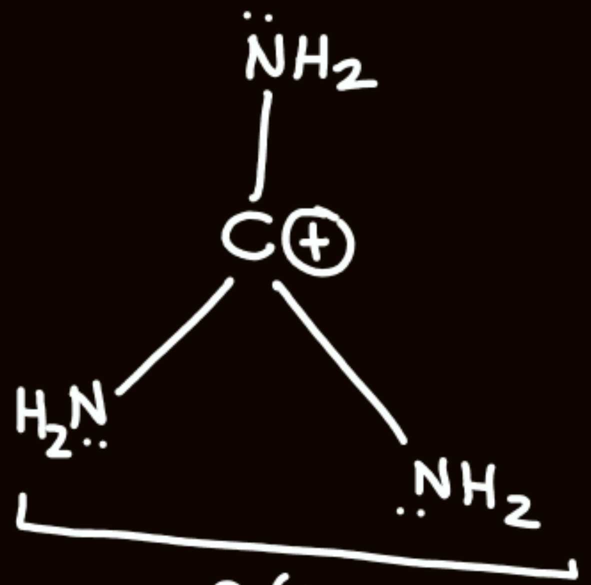
Q1 $(CH_3)_3N$ $(CH_3)_2NH$ CH_3NH_2 Base → a > b > c

Q2 $(CH_3)_3N$ $(CH_3)_2NH$ CH_3NH_2 aqueous Phase Base → b > c > a

Q3 $(Et)_3N$ $(Et)_2NH$ $EtNH_2$ (aq. state) Base → b > a > c

Guanadine base





Guanadine base
↓
Highly stable Base
↓
3 lp → 2 lp → delocalised (dlp)
→ 1 lp → localised (llp)

Unstable
+ve charge → more EN

3 (+M) group present. → So it is Highly Basic.

localised lp → lp which is not in Resonance.
delocalised lp → lp which is in Resonance.

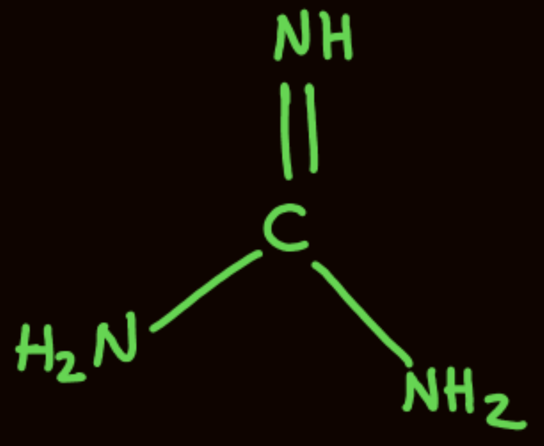
diff b/w nu⁻ & base

Nu⁻ → EDG → Electron Rich
→ donates e⁻ to any comp

Base → EDG → Electron Rich
→ donates e⁻ to H^+ only.

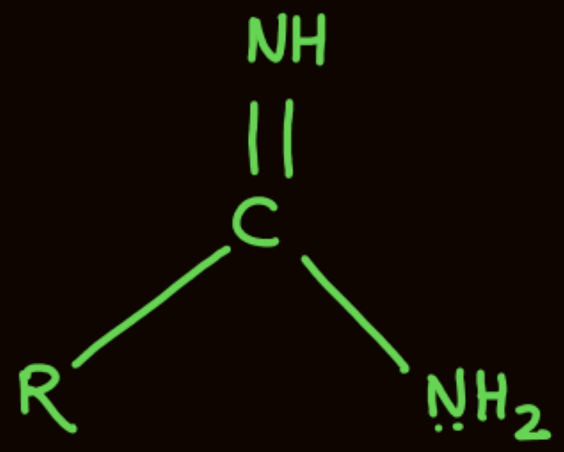
note

Basic Strength Order



Guanadine base

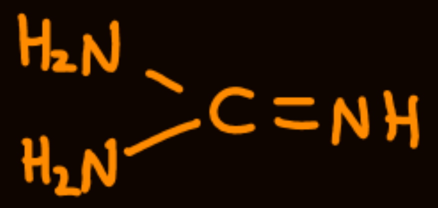
>

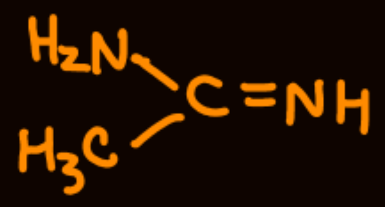


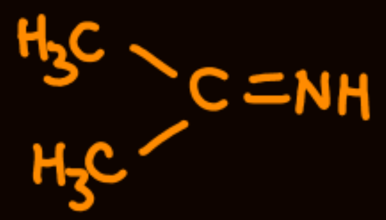
Amidine Base

> localised lp > delocalised lp

Que

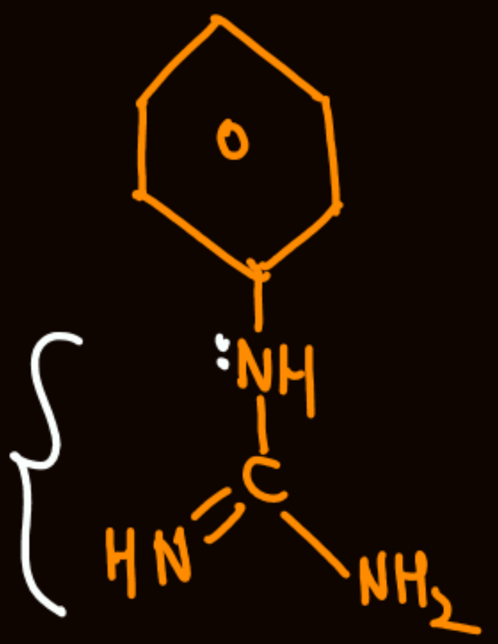


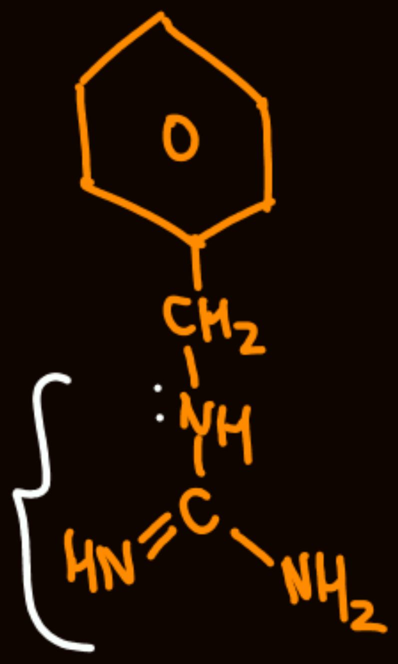




a > b > c

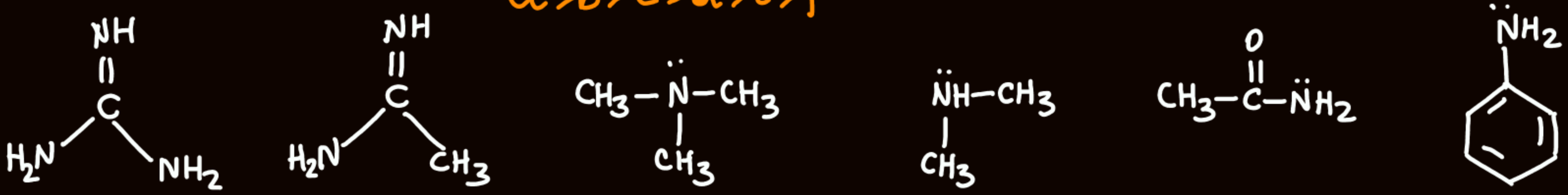
Que

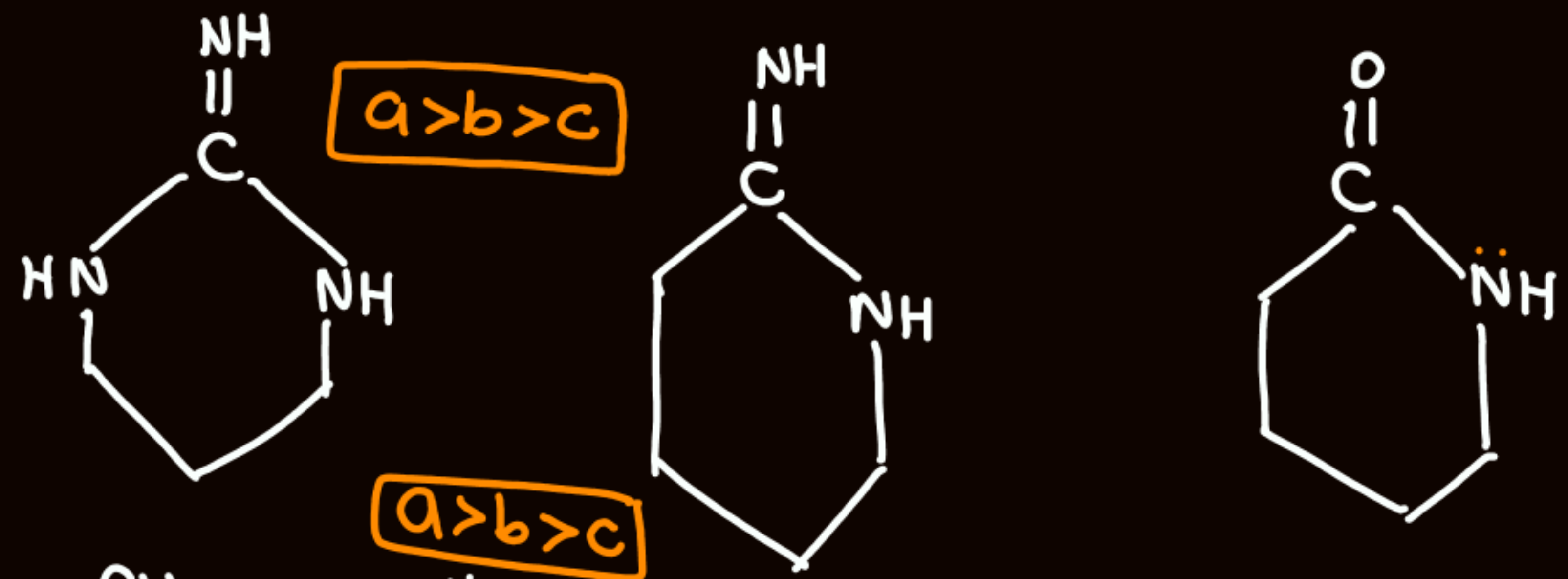




b > a

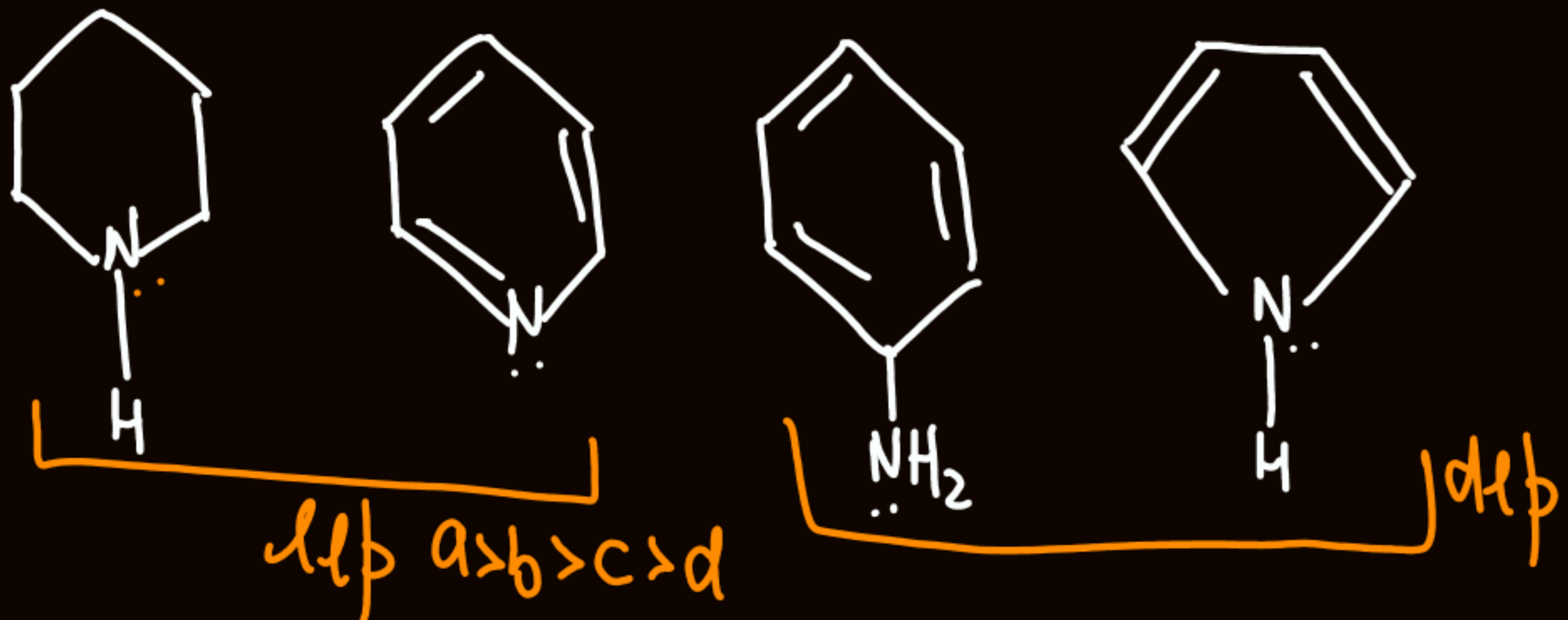
a>b>c>d>e>f



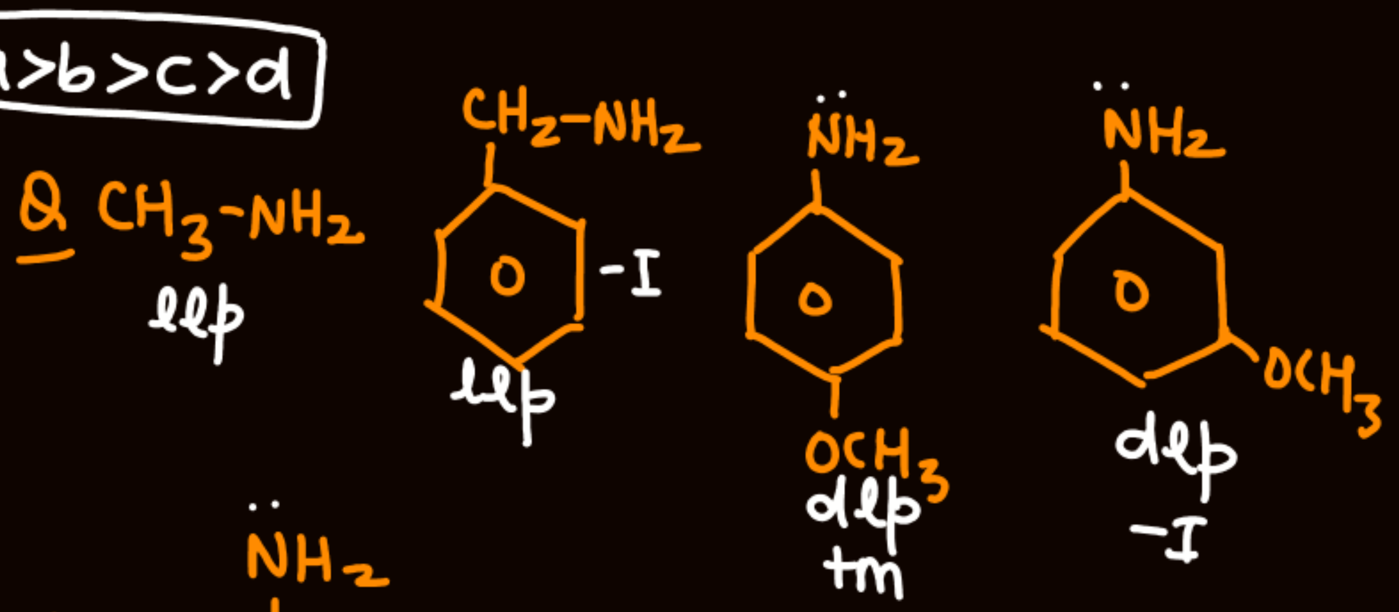


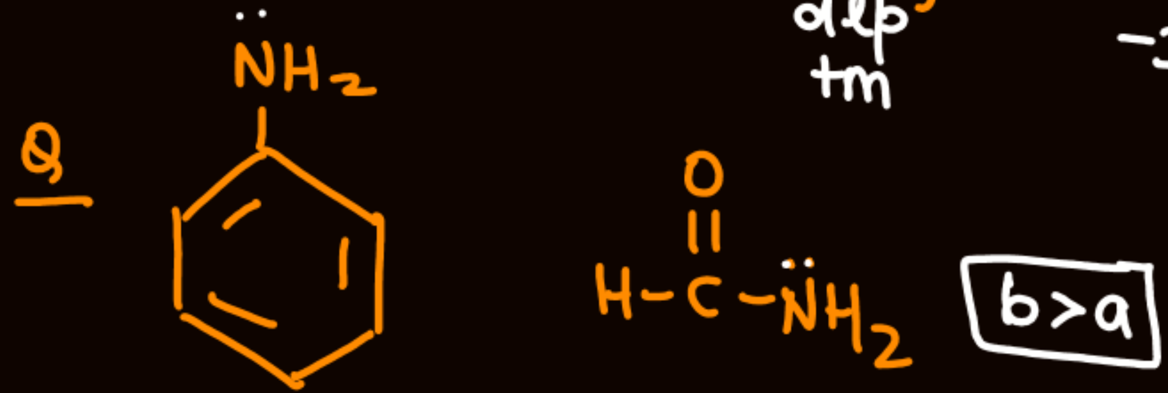
a>b>c

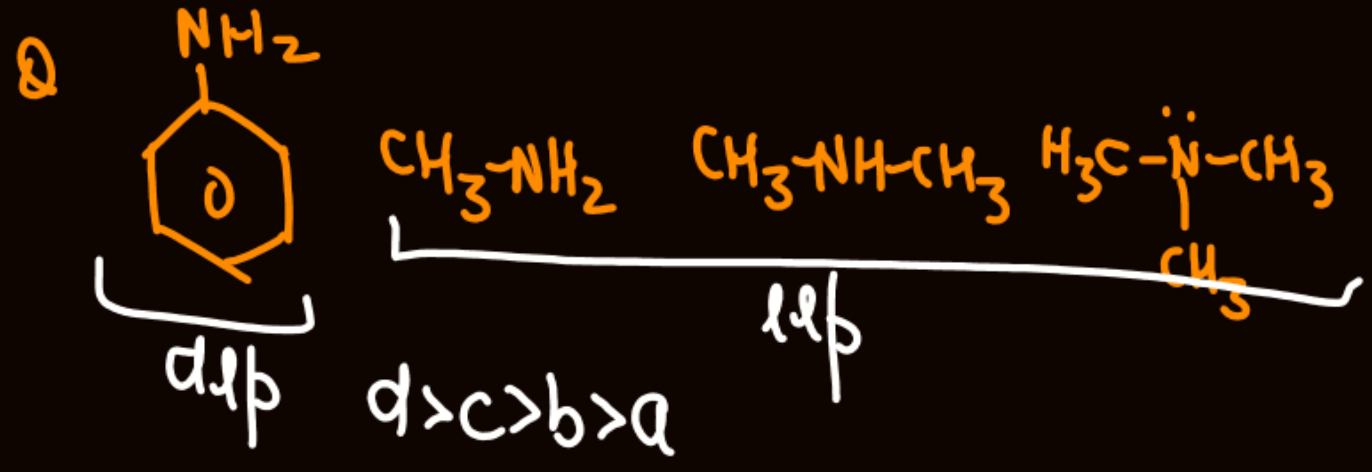
$CH_3-CH_2-\ddot{N}H_2$ $CH_3-CH=\ddot{N}H$ $CH_3-C\equiv\ddot{N}$



a>b>c>d



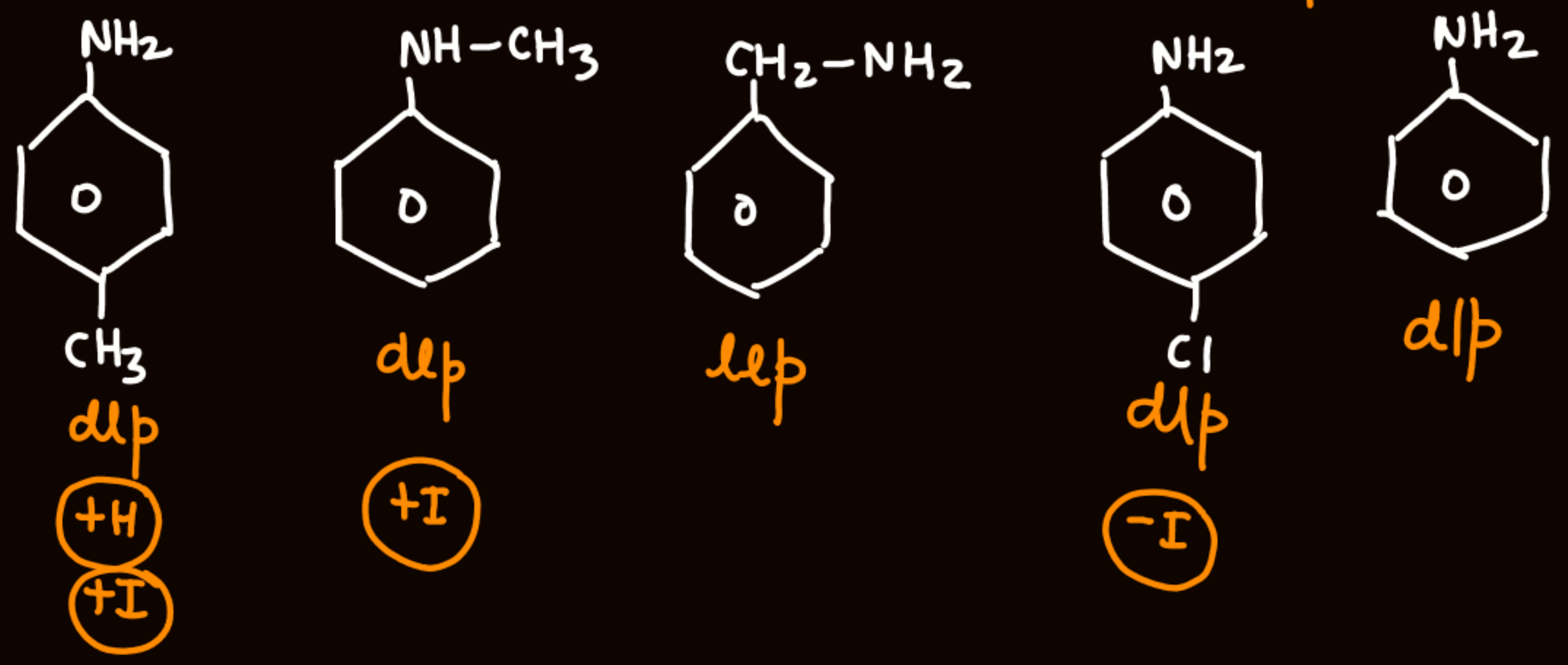




Q (a) $(Ph)_3N$ (b) $(Ph)_2NH$ (c) $(Ph)-NH_2$ (d) $Ph-CH_2-NH_2$ (lp) (e) CH_3-NH_2 (lp)

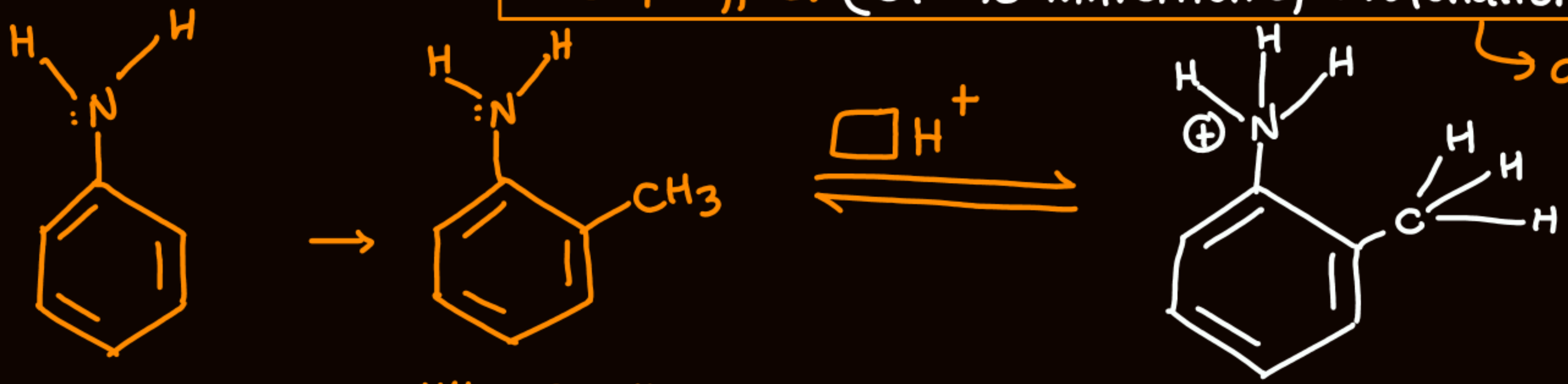
e>d>c>b>a

Q



c>a>b>e>d

SIP effect (Steric Inhibition of Protonation)



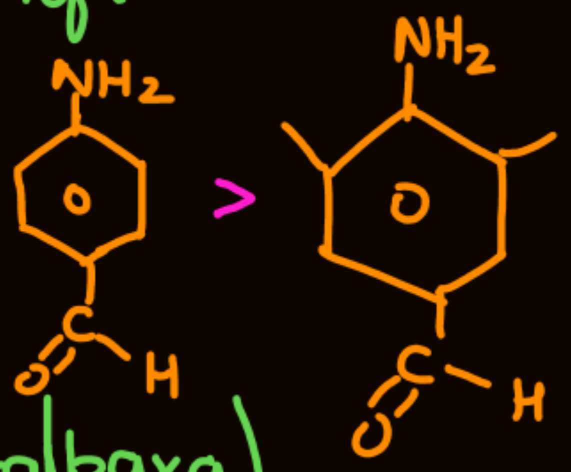
NH_2 → Small group
↓
no Repulsion

Repulsion
(Unstable)

↳ donate lp to H^+

⇒ Eq^m shifts towards left.

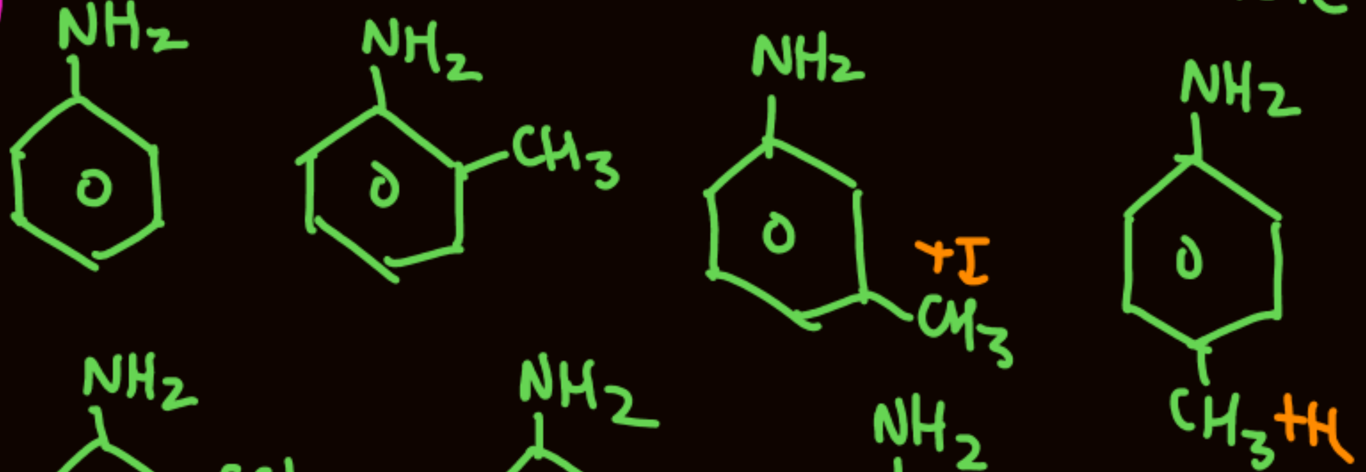
Q



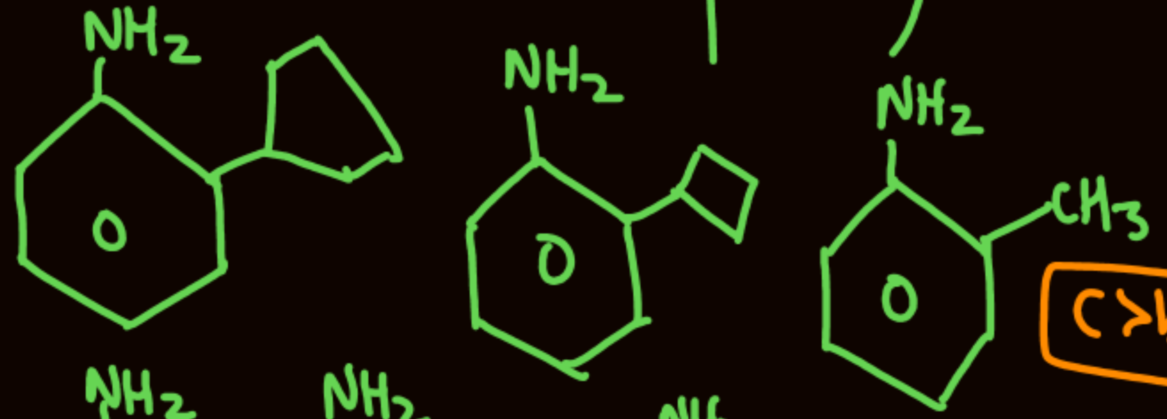
Ortho substituted aniline is less basic than its derivative (meta|para)

d>c>a>b

Q

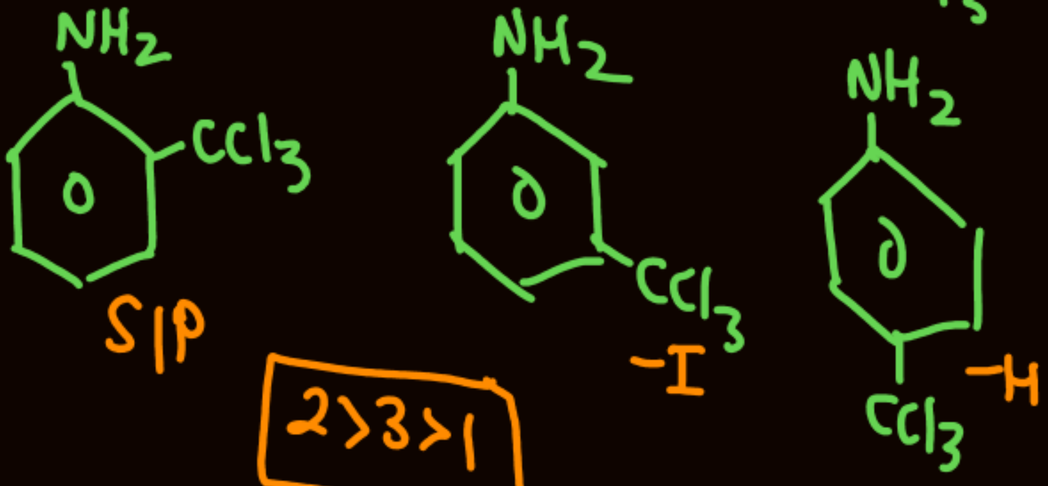


Q



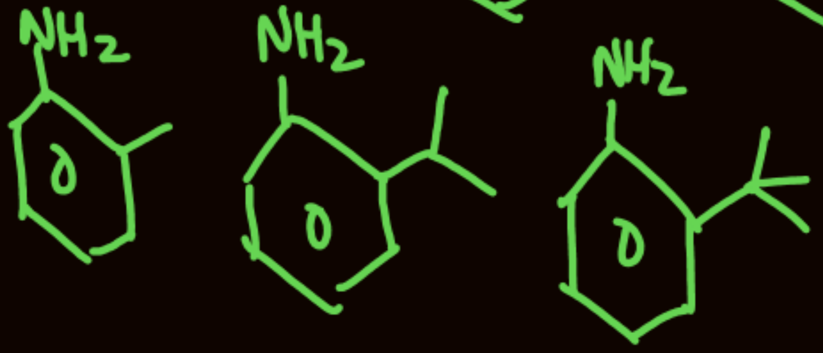
c>b>a

Q



2>3>1

Q



a>b>c

हाइड्रोकार्बन

HYDROCARBON

BOC
IUPAC
Isomerism
GOC

Hydrocarbon ← Alkane – 4, Alkene – 5, Alkyne – 3, Benzene – 1

7 → Haloalkane & Haloarene

6 → Alcohol phenol ether

6 → Aldehyde ketone carboxylic acid

3 → Amines

3 → Biomolecules

HYDROCARBON

Hydrocarbon

- Comp made of Carbon and Hydrogen is called Hydrocarbon.
- General Formula C_xH_y.
- Hydrocarbon is used as a fuel in daily life –

LPG → Liquified Petroleum Gas → methane 70% — 80%; ethane 10% — 20%; propane ~10%

CNG → Compressed Natural Gas

LNG → Liquified Natural Gas → obtained by Liquification of natural Gas.

Petroleum, Diesel, Kerosene] Fractional distillation of Petroleum.

Coal Gas] Destructive distillation of coal.

Uses of Hydrocarbon:
- → Hydrocarbon is used in manufacture of Polymer. eg Polyethene, Polypropene, Polystyrene
- → Large/Big Hydrocarbon is used in manufacture of Paint (used as solvent)

The term 'hydrocarbon' is self-explanatory which means compounds of carbon and hydrogen only. Hydrocarbons play a key role in our daily life. You must be familiar with the terms 'LPG' and 'CNG' used as fuels. LPG is the abbreviated form of liquified petroleum gas whereas CNG stands for compressed natural gas. Another term 'LNG' (liquified natural gas) is also in news these days. This is also a fuel and is obtained by liquifaction of natural gas. Petrol, diesel and kerosene oil are obtained by the fractional distillation of petroleum found under the earth's crust. Coal gas is obtained by the destructive distillation of coal. Natural gas is found in upper strata during drilling of oil wells. The gas after compression is known as compressed natural gas. LPG is used as a domestic fuel with the least pollution. Kerosene oil is also used as a domestic fuel but it causes some pollution. Automobiles need fuels like petrol, diesel and CNG. Petrol and CNG operated automobiles cause less pollution. All these fuels contain mixture of hydrocarbons, which are sources of energy. Hydrocarbons are also used for the manufacture of polymers like polythene, polypropene, polystyrene etc. Higher hydrocarbons are used as solvents for paints. They are also used as the starting materials for manufacture of many dyes and drugs. Thus, you can well understand the importance of hydrocarbons in your daily life. In this unit, you will learn more about hydrocarbons.

Classification of Hydrocarbon

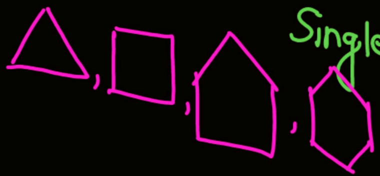
Saturated Hydrocarbon

- Hydrocarbon containing all C–C & C–H single bond.
  - C—C
  - C—H

(i) Alkane → open chain
C–C & C–H
single bond

CH_4, CH_3-CH_3, $CH_3-CH_2-CH_3$

(ii) cycloalkane → Closed chain
C–C & C–H
Single bond



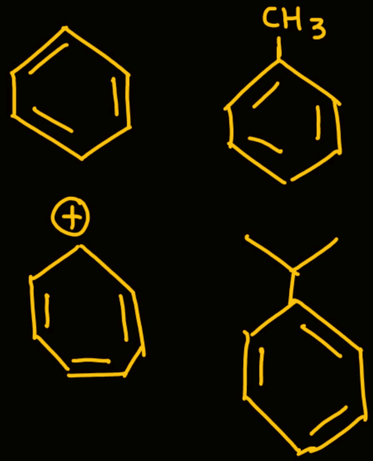
Unsaturated Hydrocarbon

- Hydrocarbon containing Carbon–Carbon multiple bonds.
  - C—H
  - C=C → alkene
  - C≡C → alkyne

$H_2C=CH_2$, $CH_3-CH=CH_2$
$CH_3-CH=CH-CH_3$,
$CH\equiv CH$, $CH_3-C\equiv CH$,
$CH_3-C\equiv C-CH_3$

Aromatic Hydrocarbon

Cyclic Hydrocarbon with alternate pi bond & which follows Huckel's Rule $(4n+2)\pi e^-$.



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9.1 CLASSIFICATION

Hydrocarbons are of different types. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories – (i) saturated (ii) unsaturated and (iii) aromatic hydrocarbons. Saturated hydrocarbons contain carbon-carbon and carbon-hydrogen single bonds. If different carbon atoms are joined together to form open chain of carbon atoms with single bonds, they are termed as alkanes as you have already studied in Unit 8. On the other hand, if carbon atoms form a closed chain or a ring, they are termed as cycloalkanes. Unsaturated hydrocarbons contain carbon-carbon multiple bonds – double bonds, triple bonds or both. Aromatic hydrocarbons are a special type of cyclic compounds. You can construct a large number of models of such molecules of both types (open chain and close chain) keeping in mind that carbon is tetravalent and hydrogen is monovalent. For making models of alkanes, you can use toothpicks for bonds and plasticine balls for atoms. For alkenes, alkynes and aromatic hydrocarbons, spring models can be constructed.

Alkanes

- Hydrocarbon containing C—C Singlebond & C—H Single bond is Called alkanes.
- General Formula → C_nH_{2n+2}
- n=1 CH_4 Methane (Marshgas) → Found in marshy places / coal mines.
  - n=2 C_2H_6 ethane
  - n=3 C_3H_8 propane
  - n=4 C_4H_{10} Butane
- Alkanes are also k/a Paraffins because they are Very less reactive bcoz of C—C & C—H Single bond (strong bond & non polar bond)
  - Paraffins: Parum → little; Affins → Affinity
  - Very less reactive: donot react with acid, base, other reagent. inert in nature
- Homologous Series →
  - CH_4
  - CH_3-CH_3
  - $CH_3-CH_2-CH_3$
  - $CH_3-CH_2-CH_2-CH_3$
  - $CH_3-CH_2-CH_2-CH_2-CH_3$

  B.P ↑ (going down the series)

  Each member of Homologous Series is Called Homologue & it differs by CH_2 Molecule.

CH_4 – Methane

- CH_4 (methane) → First member of C_nH_{2n+2} alkane series.
- Structure →



→ 4 σ bond → sp^3 Hybridisation

→ Tetrahedral Geometry

→ 109.5°

→ Bond length : C–C > C–H

C–C	C–H
2p—2p	2p—1s
Large size overlap	Small size overlap
Large bond	Small bond
↓	↓
1.54 A°	1.12 A°
154 pm	112 pm

- Overlap → sp^3 – s overlap

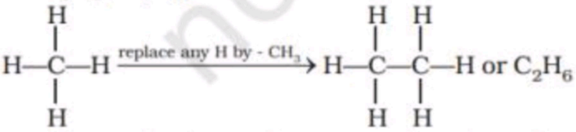
CH_4

CH_3-CH_3

$CH_3-CH_2-CH_3$

9.2 ALKANES

As already mentioned, alkanes are saturated open chain hydrocarbons containing carbon - carbon single bonds. Methane (CH_4) is the first member of this family. Methane is a gas found in coal mines and marshy places. If you replace one hydrogen atom of methane by carbon and join the required number of hydrogens to satisfy the tetravalence of the other carbon atom, what do you get? You get C_2H_6. This hydrocarbon with molecular formula C_2H_6 is known as ethane. Thus you can consider C_2H_6 as derived from CH_4 by replacing one hydrogen atom by $-CH_3$ group. Go on constructing alkanes by doing this theoretical exercise i.e., replacing hydrogen atom by $-CH_3$ group. The next molecules will be C_3H_8, C_4H_{10} …



These hydrocarbons are inert under normal conditions as they do not react with acids, bases and other reagents. Hence, they were earlier known as paraffins (*latin* : *parum*, little; *affinis*, affinity). Can you think

of the general formula for alkane family or **homologous series**? If we examine the formula of different alkanes we find that the general formula for alkanes is C_nH_{2n+2}. It represents any particular homologue when *n* is given appropriate value. Can you recall the structure of methane? According to VSEPR theory (Unit 4), methane has a tetrahedral structure (Fig. 9.1), in which carbon atom lies at the centre and the four hydrogen atoms lie at the four corners of a regular tetrahedron. All H-C-H bond angles are of 109.5 .

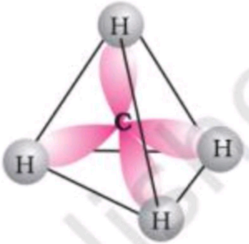


Fig. 9.1 *Structure of methane*

In alkanes, tetrahedra are joined together in which C-C and C-H bond lengths are 154 pm and 112 pm respectively (Unit 8). You have already read that C–C and C–H σ bonds are formed by head-on overlapping of sp^3 hybrid orbitals of carbon and 1s orbitals of hydrogen atoms.

Isomerism of alkane

\# $\overset{1°}{C}H_4$, $\overset{1°}{C}H_3-\overset{1°}{C}H_3$, $\overset{1°}{C}H_3-\overset{2°}{C}H_2-\overset{1°}{C}H_3$ (First 3 member of alkane → donot show str isomerism)

\# C_4H_{10} (butane) → $\overset{1°}{C}H_3-\overset{2°}{C}H_2-\overset{2°}{C}H_2-\overset{1°}{C}H_3$ (n-butane) BP more → Chain isomer

→ $\overset{1°}{C}H_3-\overset{3°}{C}H(\overset{1°}{C}H_3)-\overset{1°}{C}H_3$ (Iso-butane) BP less

2 Str Isomer

$B.P \propto \frac{1}{Branching}$

\# C_5H_{12} (Pentane) → $\overset{1°}{C}H_3-\overset{2°}{C}H_2-\overset{2°}{C}H_2-\overset{2°}{C}H_2-\overset{1°}{C}H_3$ (n-pentane)

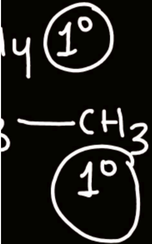
$\overset{1°}{C}H_3-\overset{3°}{C}H(\overset{1°}{C}H_3)-\overset{2°}{C}H_2-\overset{1°}{C}H_3$ (Iso-pentane)

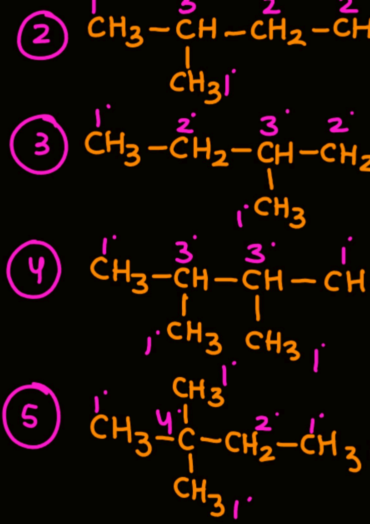
$\overset{1°}{C}H_3-\overset{4°}{C}(\overset{1°}{C}H_3)(\overset{1°}{C}H_3)-\overset{1°}{C}H_3$ (neo-pentane)

3 Str Isomers

BP → n-pentane > Isopentane > neo pentane

→ Chain isomer





Iso hexane
2-methylpentane

3-methyl pentane

(Vicinal)
2,3-dimethyl butane

neohexane
(geminal)
2,2-dimethylbutane

1,2 — Cl
1,3 — Cl
1,4 — Cl
1,5 — Cl
2,3 — PI
2,4 — Cl
2,5 — Cl
3,4 — Cl
3,5 — CI
4,5 → PI

Degree of Carbon —

① 1°/Primary Carbon → If Carbon is not bonded/bonded to 1 another Carbo
↳ Terminal Carbon is always 1°.

② 2°/Secondary Carbon → Carbon is bonded to 2 Carbon.

③ 3°/Tertiary Carbon → Carbon is bonded to 3 Carbon.

④ 4°/Quatanary Carbon → Carbon is bonded to 4 Carbon.

Isomerism chart

$CH_4 \longrightarrow 0$

$C_2H_6 \longrightarrow 0$

$C_3H_8 \longrightarrow 0$

$C_4H_{10} \longrightarrow 2$

$C_5H_{12} \longrightarrow 3$

$C_6H_{14} \longrightarrow 5$

$C_7H_{16} \longrightarrow 9$

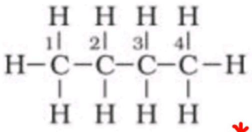
⋮

$C_{10}H_{22} \longrightarrow 75$

9.2.1 Nomenclature and Isomerism

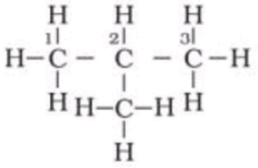
You have already read about nomenclature of different classes of organic compounds in Unit 8. Nomenclature and isomerism in alkanes can further be understood with the help of a few more examples. Common names are given in parenthesis. First three alkanes – methane, ethane and propane have only one structure but higher alkanes can have more than one structure. Let us write structures for C_4H_{10}. Four carbon atoms of C_4H_{10} can be joined either in a continuous chain or with a branched chain in the following two ways :

I



Butane (*n*- butane), (b.p. 273 K)

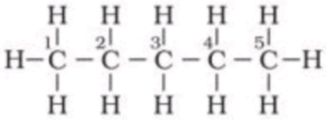
II



2-Methylpropane (isobutane)
(b.p.261 K)

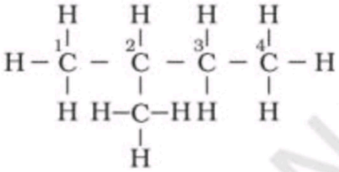
In how many ways, you can join five carbon atoms and twelve hydrogen atoms of C_5H_{12}? They can be arranged in three ways as shown in structures III–V

III



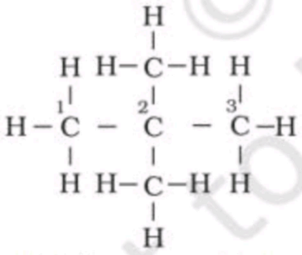
Pentane (*n*-pentane)
(b.p. 309 K)

IV



2-Methylbutane (isopentane)
(b.p. 301 K)

(V)



2,2-Dimethylpropane (neopentane)
(b.p. 282.5 K)

Structures I and II possess same molecular formula but differ in their boiling points and other properties. Similarly structures III, IV and V possess the same molecular formula but have different properties. Structures I and II are isomers of butane, whereas structures III, IV and V are isomers of pentane. Since difference in properties is due to difference in their structures, they are known as **structural isomers**. It is also clear that structures I and III have continuous chain of carbon atoms but structures II, IV and V have a branched chain. Such structural isomers which differ in chain of carbon atoms are known as **chain isomers**. Thus, you have seen that C_4H_{10} and C_5H_{12} have two and three chain isomers respectively.

Problem 9.1

Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Also write their IUPAC names.

Based upon the number of carbon atoms attached to a carbon atom, the carbon atom is termed as primary (1), secondary (2), tertiary (3) or quaternary (4). Carbon atom attached to no other carbon atom as in methane or to only one carbon atom as in ethane is called primary carbon atom. Terminal carbon atoms are always primary. Carbon atom attached to two carbon atoms is known as secondary. Tertiary carbon is attached to three carbon atoms and neo or quaternary carbon is attached to four carbon atoms. Can you identify 1 , 2 , 3 and 4 carbon atoms in structures I to V ? If you go on constructing structures for higher alkanes, you will be getting still larger number of isomers. C_6H_{14} has got five isomers and C_7H_{16} has nine. As many as 75 isomers are possible for $C_{10}H_{22}$.

Radical

Remove Hydrogen from Hydrogen from Hydrocarbon → You will get radical.

↓

General Formula → C_nH_{2n+1}

name → Alkyl

$CH_4 \xrightarrow{-H} -CH_3$ (Methyl)

$CH_3-CH_3 \xrightarrow{-H} -CH_2-CH_3$ (Ethyl)

$CH_3-CH_2-CH_3 \xrightarrow{-H} -CH_2-CH_2-CH_3$ (n-propyl)

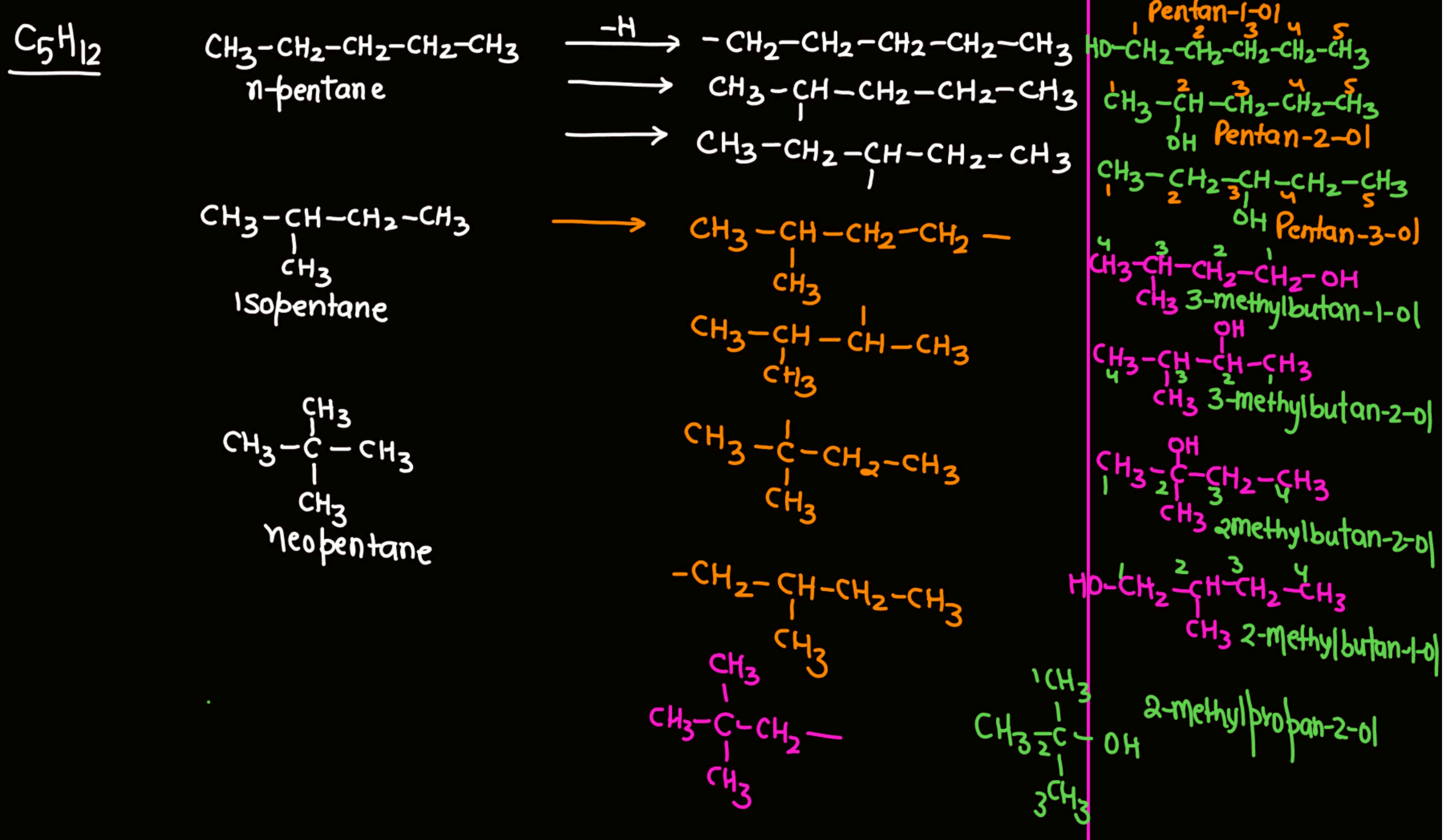
$CH_3-CH(-)-CH_3$ (Iso-propyl)

$CH_3-CH_2-CH_2-CH_3 \xrightarrow{-H} -CH_2-CH_2-CH_2-CH_3$ (n-butyl)

$CH_3-CH(-)-CH_2-CH_3$ (Sec-butyl)

$CH_3-CH(CH_3)-CH_3 \xrightarrow{-H} CH_3-CH(CH_3)-CH_2-$ (Isobutyl)

$CH_3-C(-)(CH_3)-CH_3$ (Tert butyl)



C5H12
n-pentane
Isopentane
neopentane
-H
Pentan-1-ol
Pentan-2-ol
Pentan-3-ol
3-methylbutan-1-ol
3-methylbutan-2-ol
2methylbutan-2-ol
2-methylbutan-1-ol
2-methylpropan-2-ol

In structures II, IV and V, you observed that $-CH_3$ group is attached to carbon atom numbered as 2. You will come across groups like $-CH_3$, $-C_2H_5$, $-C_3H_7$ etc. attached to carbon atoms in alkanes or other classes of compounds. These groups or substituents are known as alkyl groups as they are derived from alkanes by removal of one hydrogen atom. General formula for alkyl groups is C_nH_{2n+1} (Unit 8).

Let us recall the general rules for nomenclature already discussed in Unit 8. Nomenclature of substituted alkanes can further be understood by considering the following problem:

Problem 9.2

Write structures of different isomeric alkyl groups corresponding to the molecular formula C_5H_{11}. Write IUPAC names of alcohols obtained by attachment of –OH groups at different carbons of the chain.

Catalytic Hydrogenation

- Addition of Hydrogen to unsaturated Comp in presence of Catalyst to form Saturated Comp is known as Catalytic Hydrogenation.

$$CH_3-CH=CH_2 \xrightarrow[Ni/Pd/Pt]{H_2} CH_3-CH_2-CH_3 \rightarrow \text{Energy release}$$

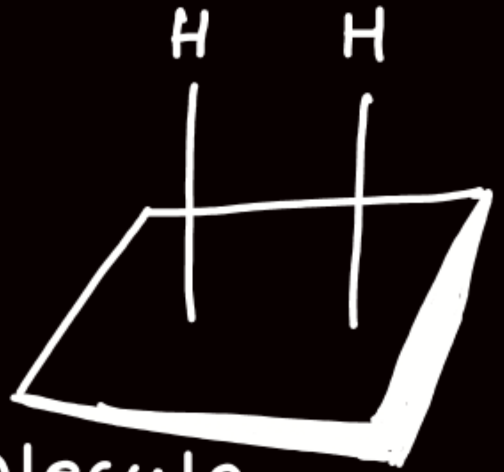
$CH_3-CH=CH_2$	$CH_3-CH_2-CH_3$
Unsaturated Comp	Saturated comp
double/triple bond	Single bond
weak bond	Strong bond
Unstable	Stable

Energy release (Heat of Hydrogenatn)
↓
Exothermic
↓
$\Delta H = -ve$
↓
$\Delta H < 0$

- $H_2 / Ni \xrightarrow{200\text{-}300^\circ C}$ (Sabatier & sanderen's Reaction)
- $H_2 | Pd, Pt \xrightarrow{\text{Room Temp}}$
- Hydrogen is added from same side. (Syn addition)

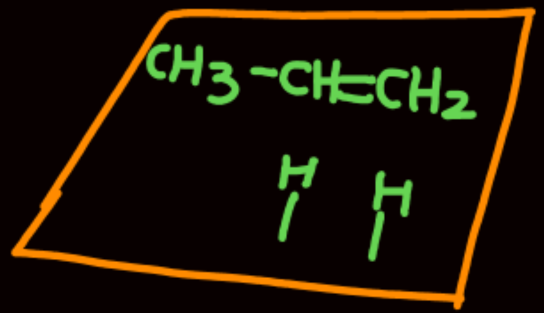
Mechanism

$$CH_3-CH=CH_2 \xrightarrow[Ni/Pd/Pt]{H_2} CH_3-\underset{H}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}$$

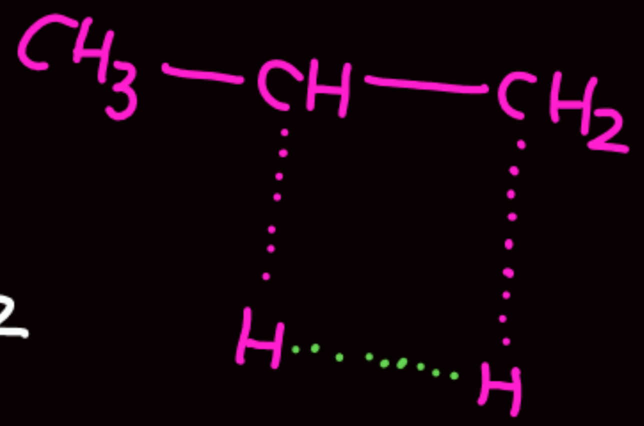


Step1 → H_2 gets adsorbed on catalyst surface.

Step2 → catalyst provides surface for Reacting molecule.



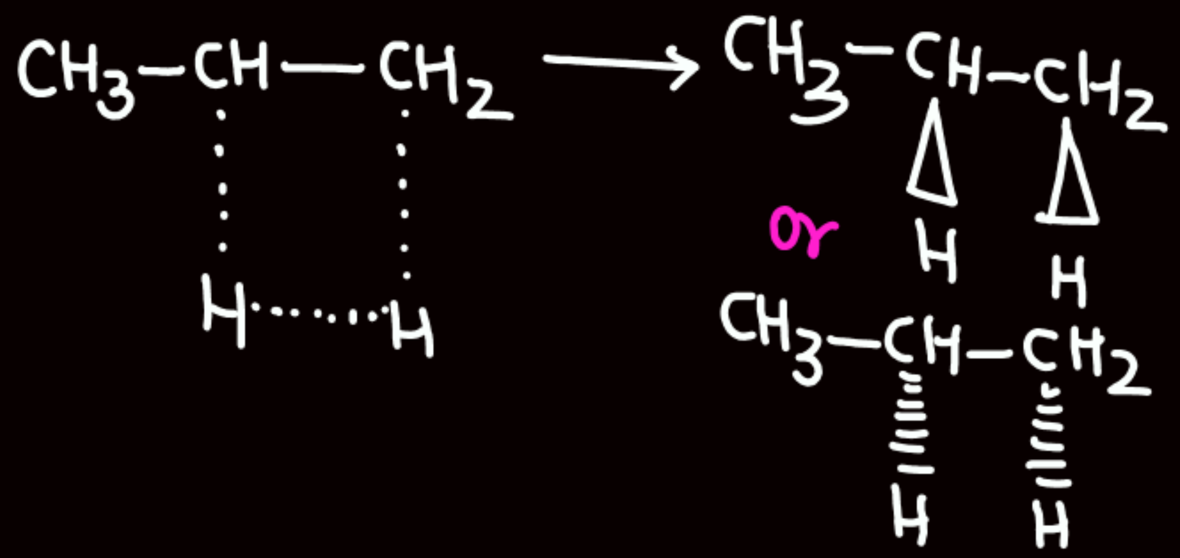
Step 3 → 4 member cyclic Transition state is formed & Hydrogen is added from same side. (Syn addition of H_2)



\# CH_4 (methane) can not be formed.

Eg

$$CH_3-CH=CH_2 \xrightarrow[Ni/Pd/Pt]{H_2}$$



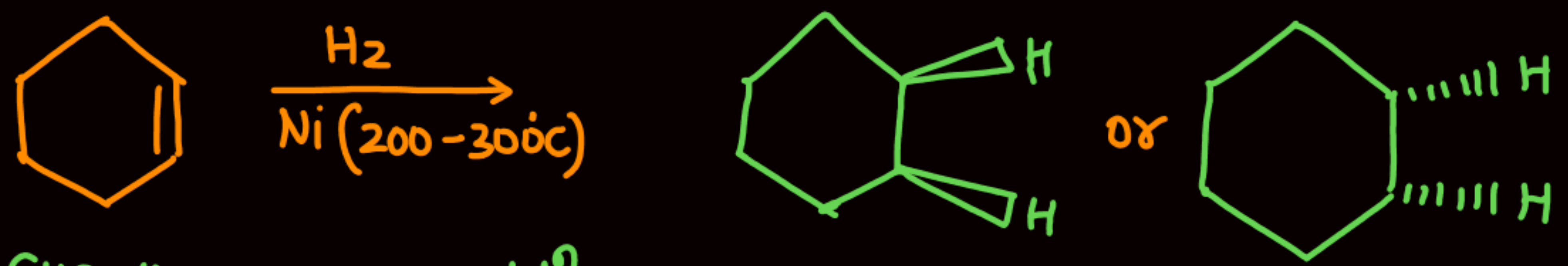
Conclusion :

Cys alkene + Syn addition → Meso

Trans alkene + Syn addition → Racemic Mix

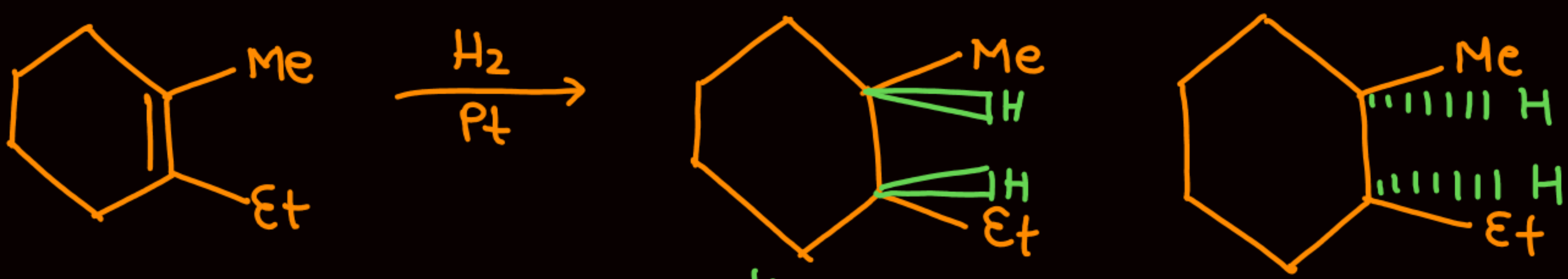
C S M
T S R

Q1

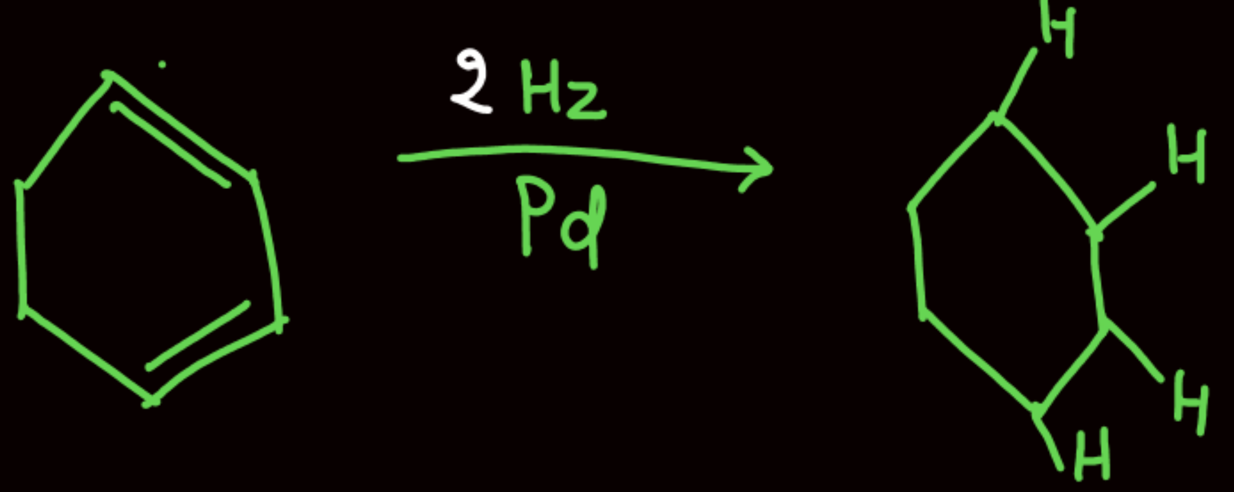


Cys alkene   Syn add^n   Meso

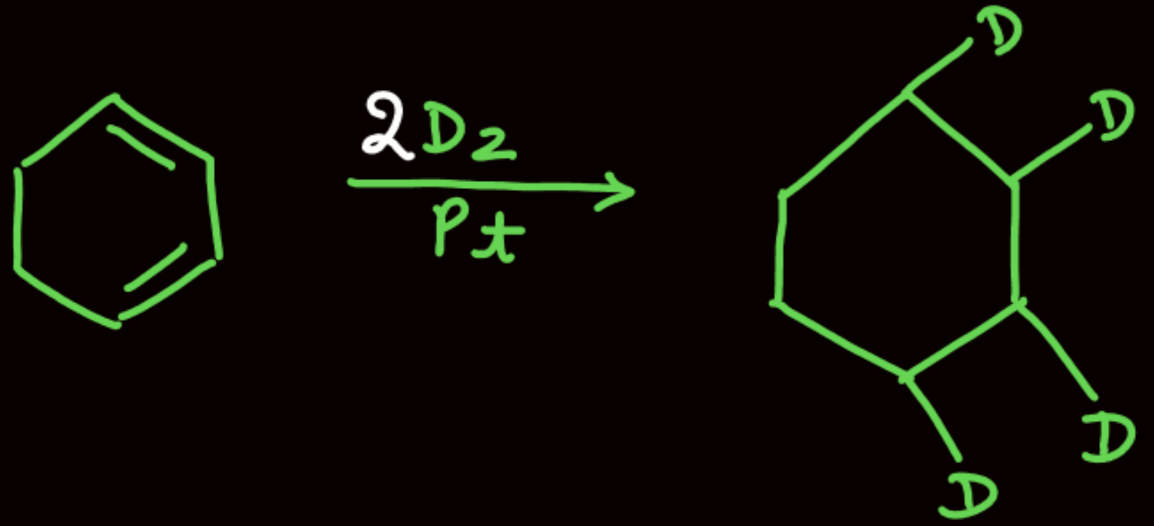
Q2



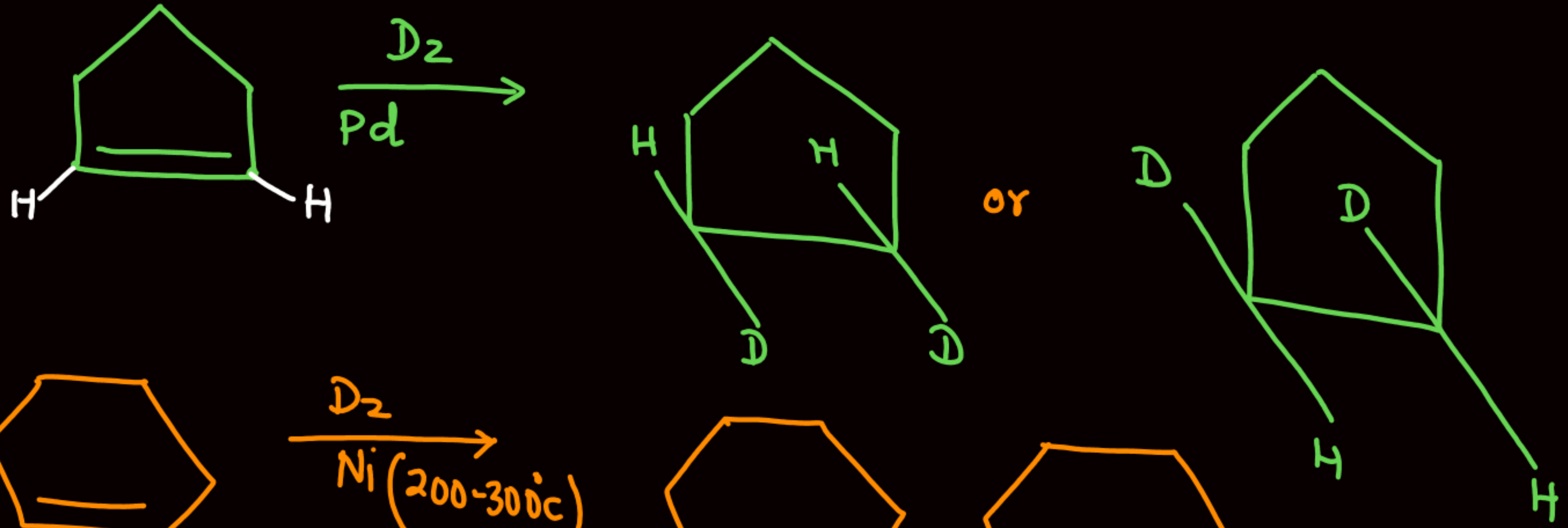
Q3



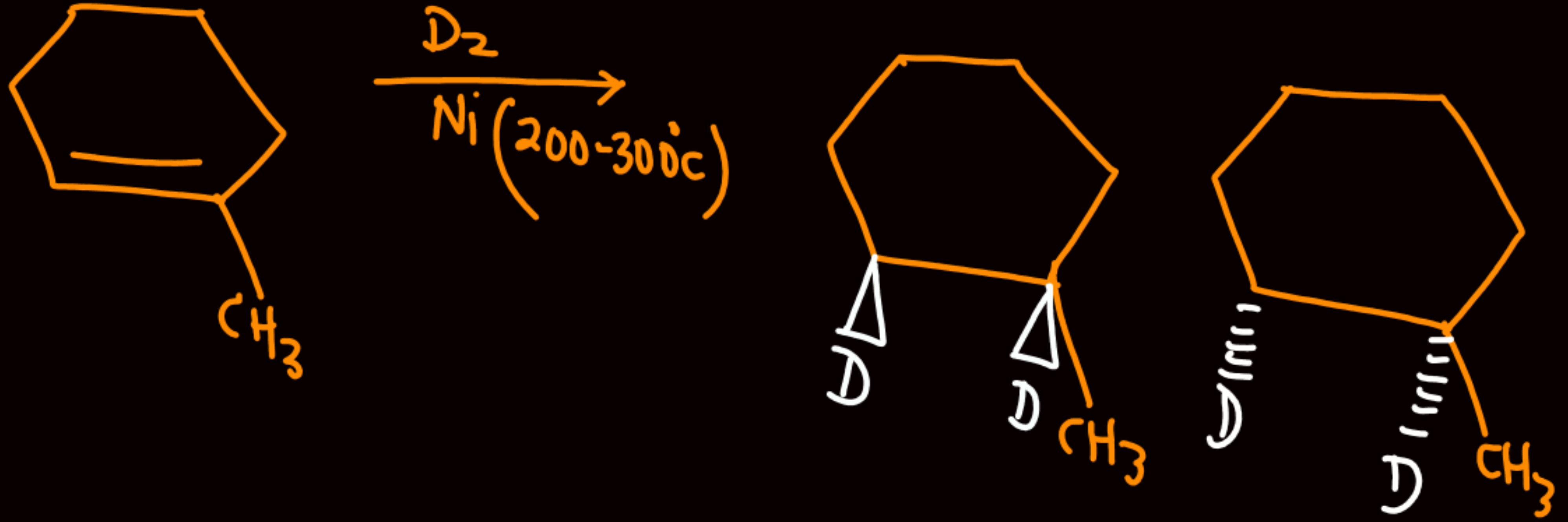
Que



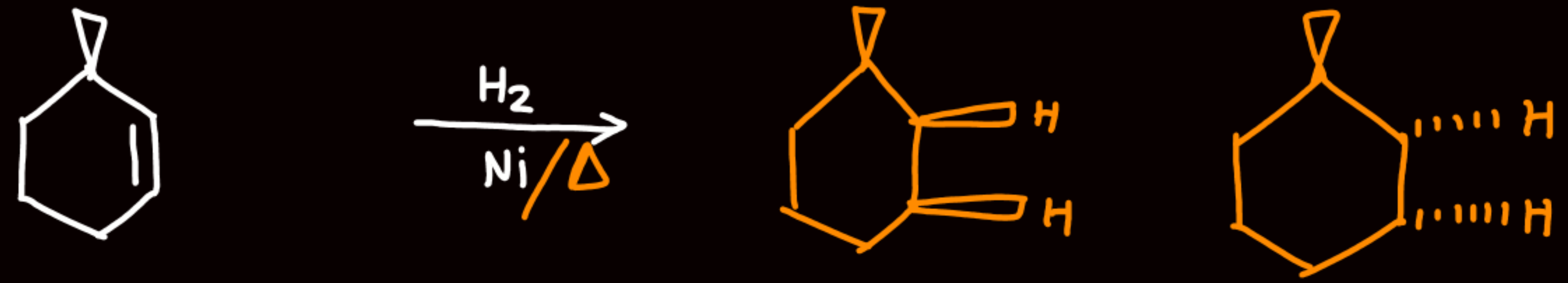
Que



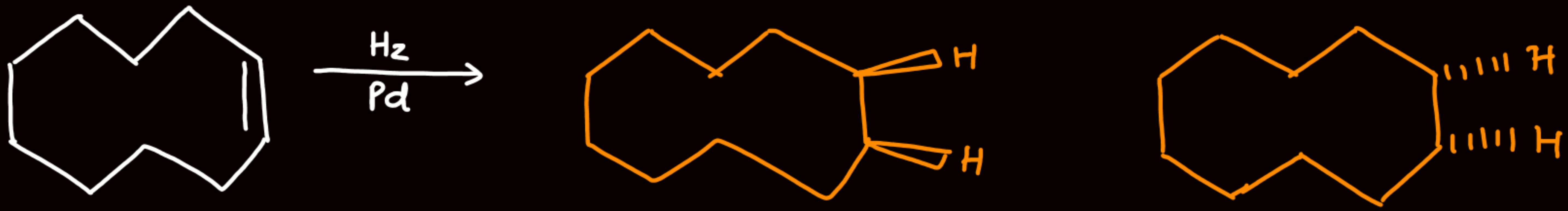
Que



Q



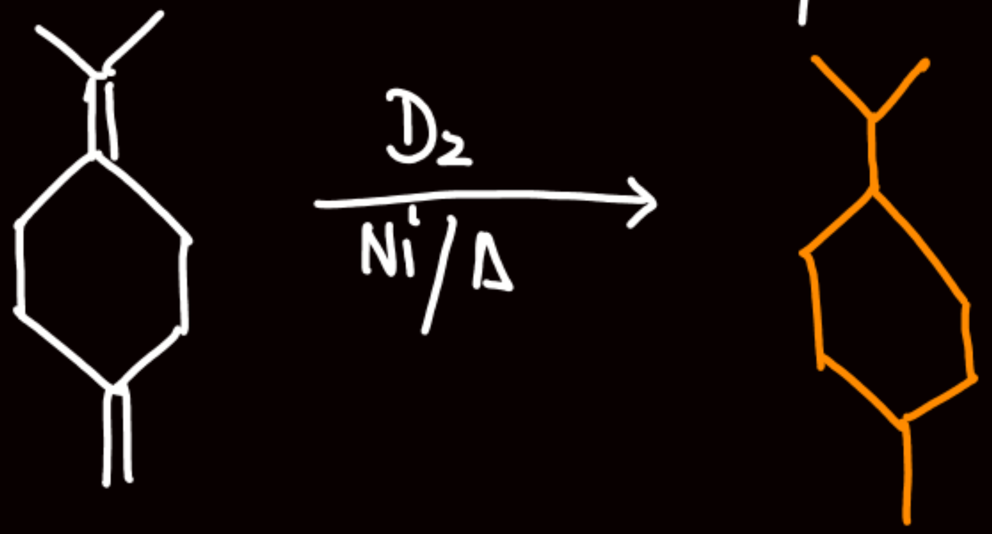
Q



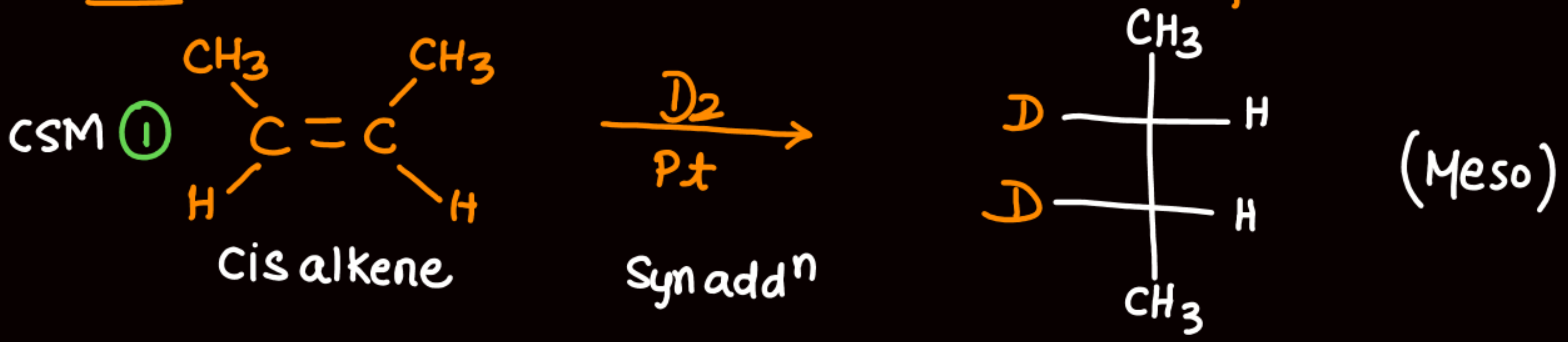
Q $CH_3-C\equiv CH \xrightarrow[Ni/\Delta]{2H_2} CH_3-CH_2-CH_3$

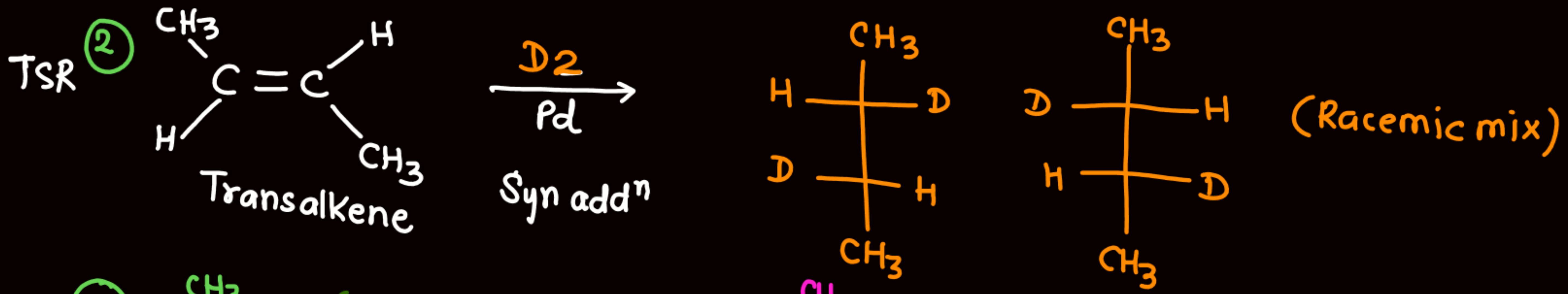
Q $CH_3-CH=CH-C\equiv CH \xrightarrow[Ni/\Delta]{3H_2} CH_3-CH_2-CH_2-CH_2-CH_3$

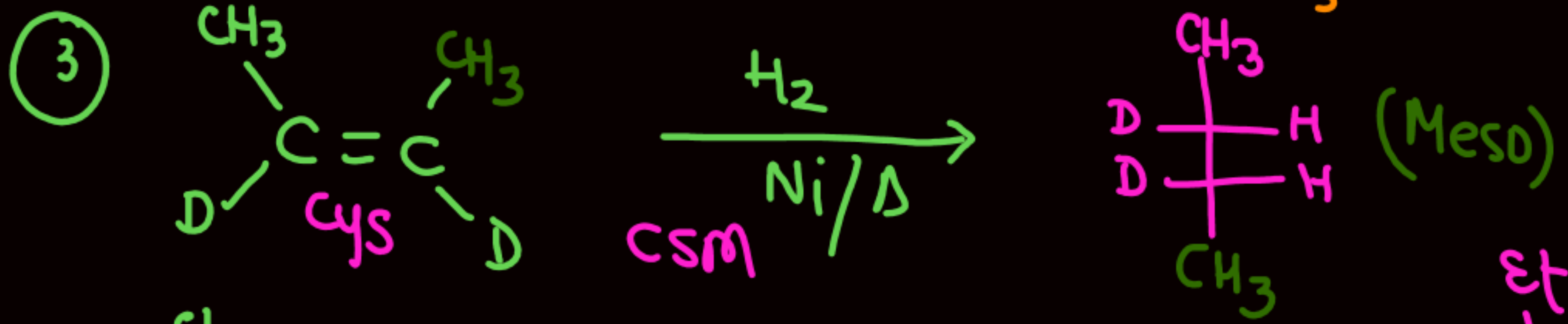
Q

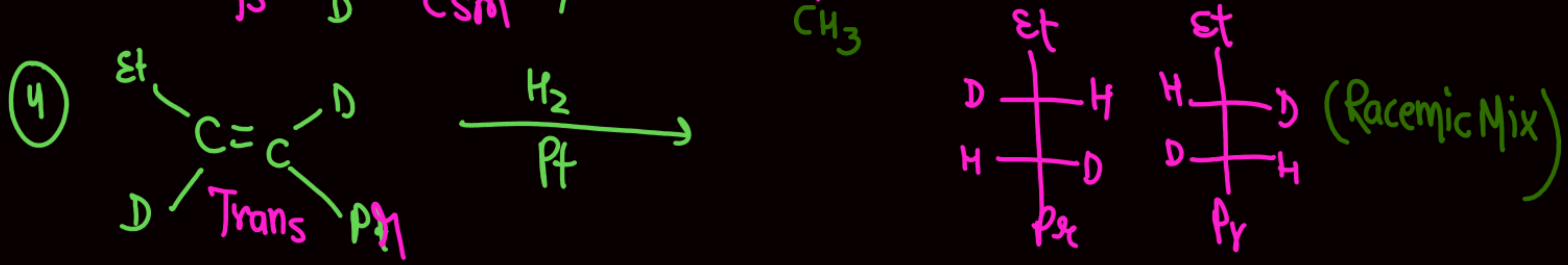


Que Find the Stereochemistry of Product formed in reaction —

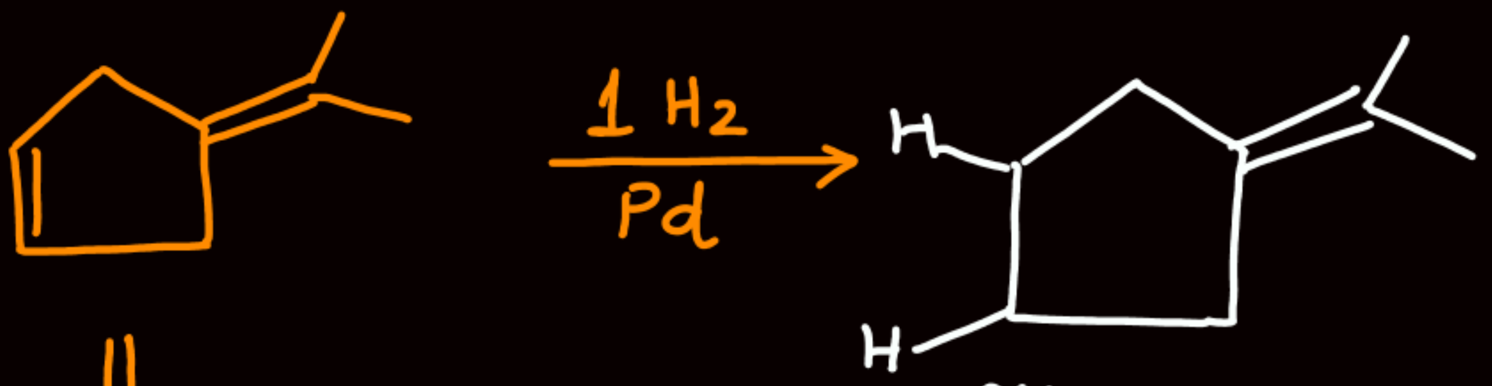


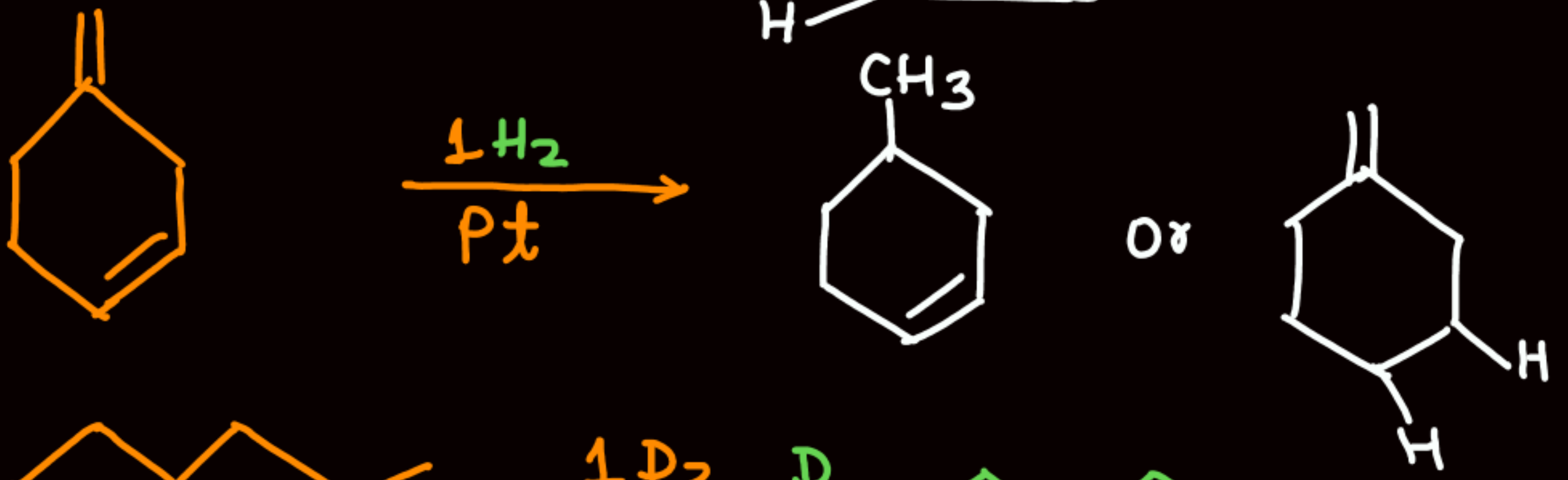


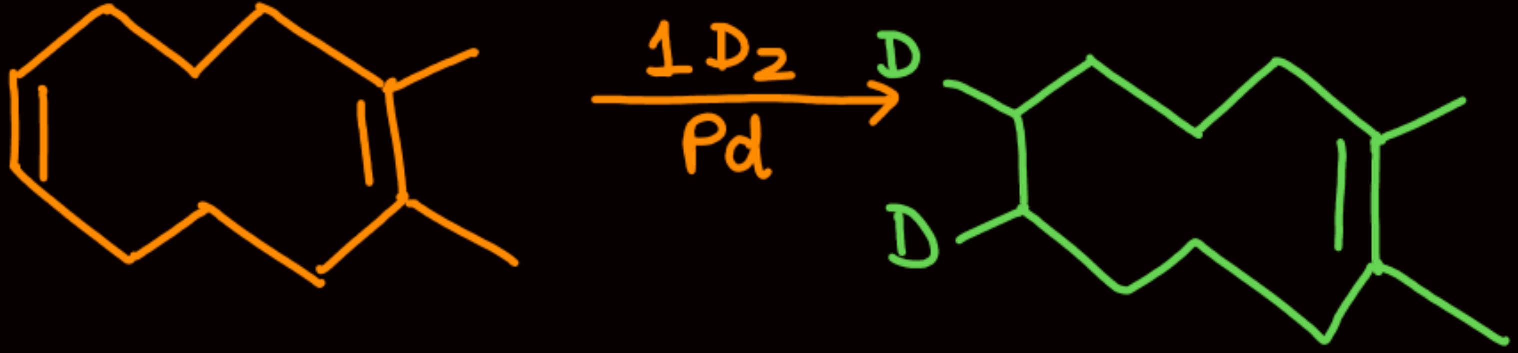


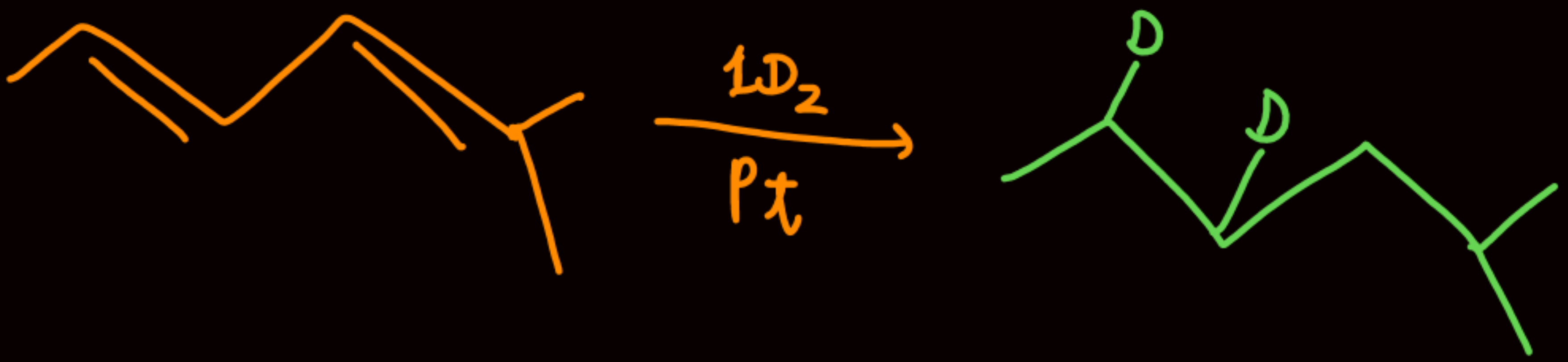


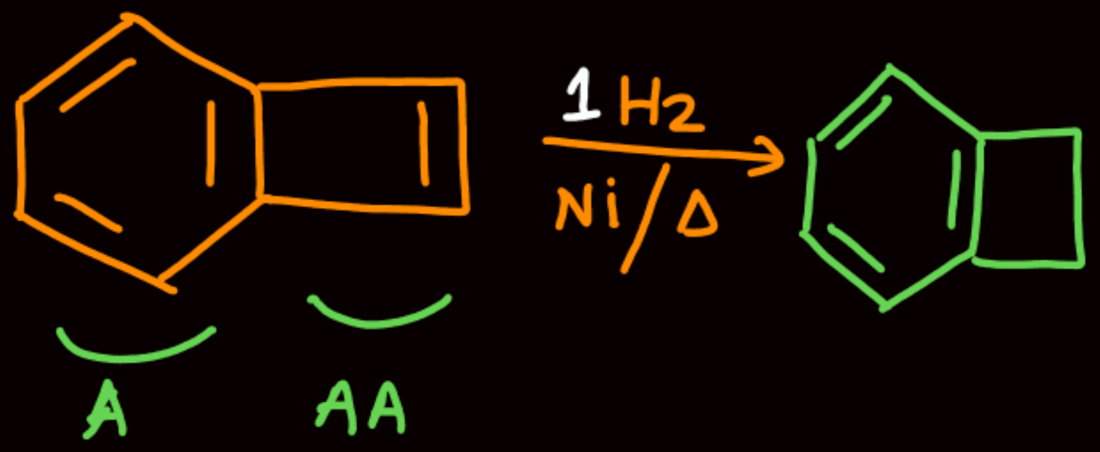
Que Find the product – (Less stable alkene will react first)











ALKYL Halide → Alkane

R—F → donot give reaction because of strong bond (Small Size overlap)

R—Cl, R—Br, R—I → They Can give reaction.

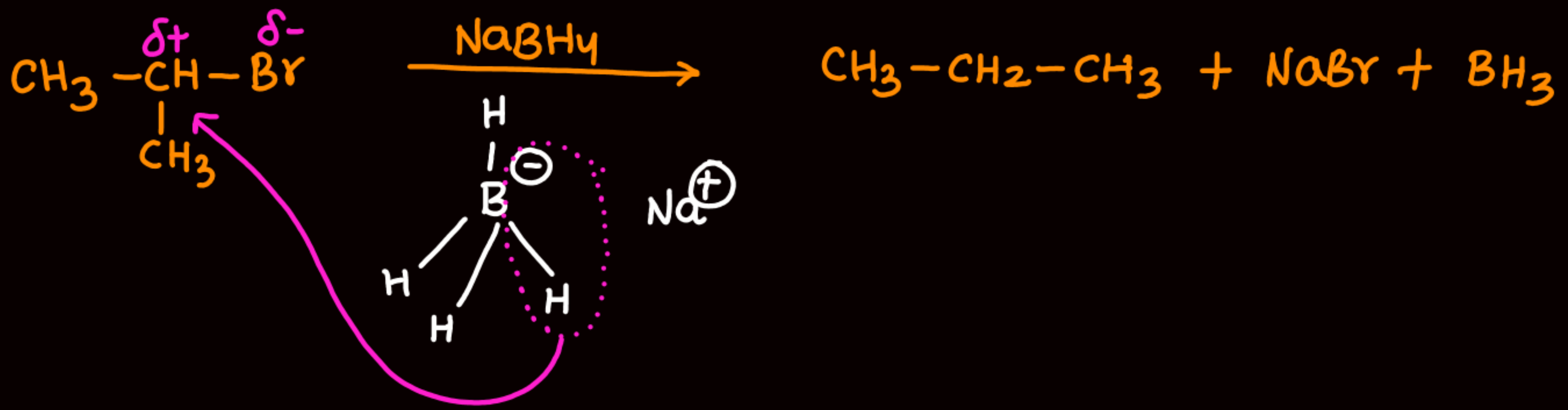
(i) Reducing agent

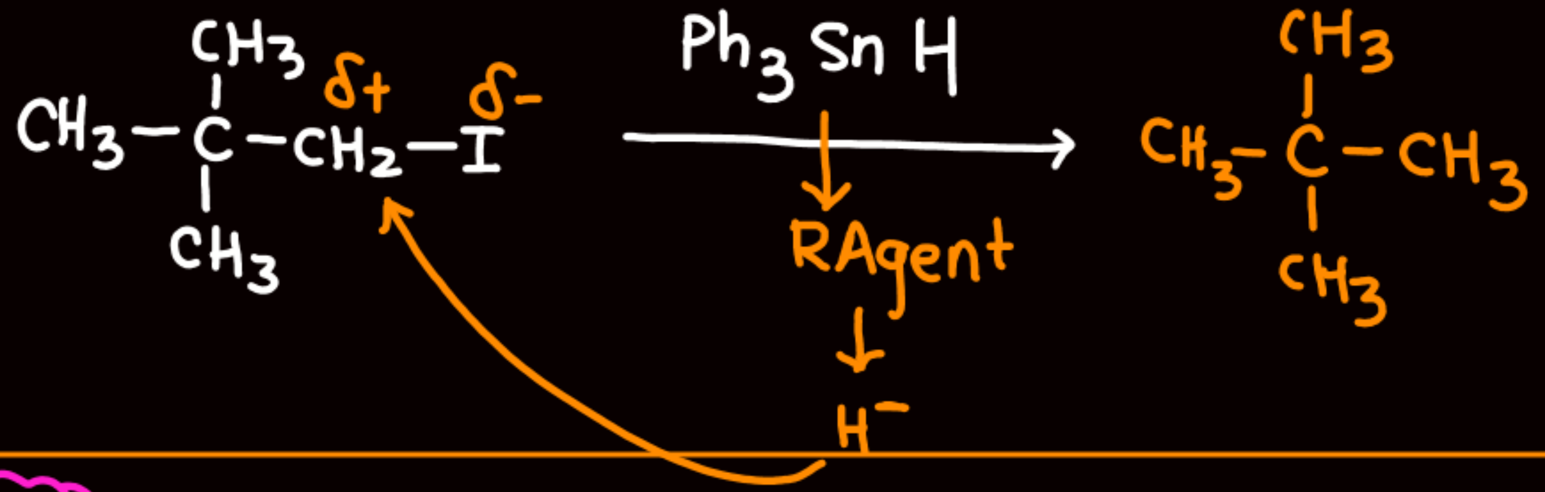
1. $LiAlH_4$ lithium aluminium Hydride [LAH]
2. $NaBH_4$ Sodium Boro Hydride [NBH]
3. Ph_3SnH Triphenyl Tin Hydride

} Reducing agent always gives H^-

$$\overset{\delta+}{CH_3-CH_2}-\overset{\delta-}{Cl} \xrightarrow{LiAlH_4} CH_3-CH_3 + LiCl + AlH_3$$







Note → $NaBH_4$, Ph_3SnH → Can reduce 1°, 2°, 3° alkyl halide → alkane

$LiAlH_4$ → Can reduce → 1°, 2° alkyl halide → alkane

→ makes alkene with 3° alkyl halide → alkene

Que

$\overset{}{CH_3-CH_2-\overset{\delta+}{CH_2}-\overset{\delta-}{Cl}}$

1° alkyl halide

$\xrightarrow{LiAlH_4}$ $CH_3-CH_2-CH_3$

$\xrightarrow{NaBH_4}$ "

$\xrightarrow{Ph_3SnH}$ "

$NaBH_4$, Ph_3SnH, $LiAlH_4$ ~~2°/3°~~

Que

$CH_3-CH_2-\overset{\delta+}{CH}(CH_3)-\overset{\delta-}{Cl}$

2° alkyl halide

$\xrightarrow{LiAlH_4}$ $CH_3-CH_2-CH_2-CH_3$

$\xrightarrow{NaBH_4}$ "

$\xrightarrow{Ph_3SnH}$ "

Que

$CH_3-CH_2-C(CH_3)_2-Cl$

3° alkyl halide

$\xrightarrow{LiAlH_4}$ $CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}=CH_2$ (minor) , $CH_3-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$ Stable (major)

$\xrightarrow{NaBH_4}$ $CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$

$\xrightarrow{Ph_3SnH}$ "

Alkyl Halide ⟶ Alkane

Metal + acid
- $Zn + HCl$
- $Zn + KOH$
- $Zn + CH_3COOH$

$$CH_3-CH_2-Cl \xrightarrow{Zn + HCl} CH_3-CH_3 + ZnCl_2$$

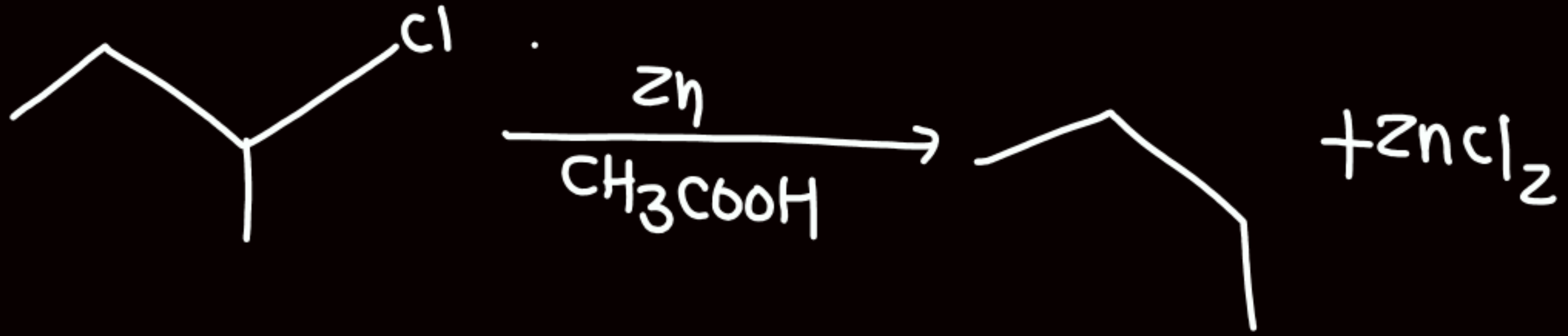
Mechanism

$$\overset{}{CH_3}-\overset{\delta+}{CH_2}-\overset{\delta-}{Cl}$$

$$Zn \longrightarrow Zn^{+2} + 2e^-$$

$$\longrightarrow CH_3-\overset{\ominus}{CH_2} \xrightarrow{HCl} CH_3-CH_3 + ZnCl_2$$

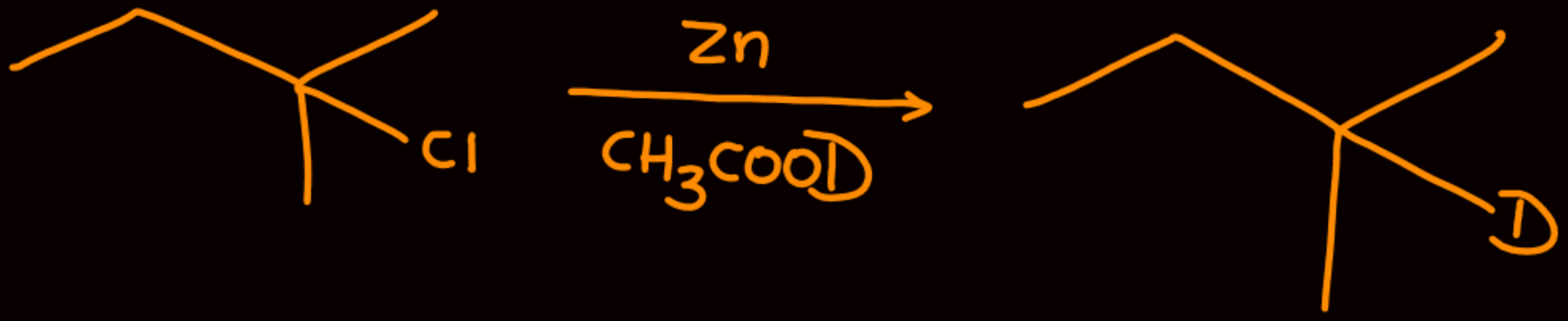
Que



Que



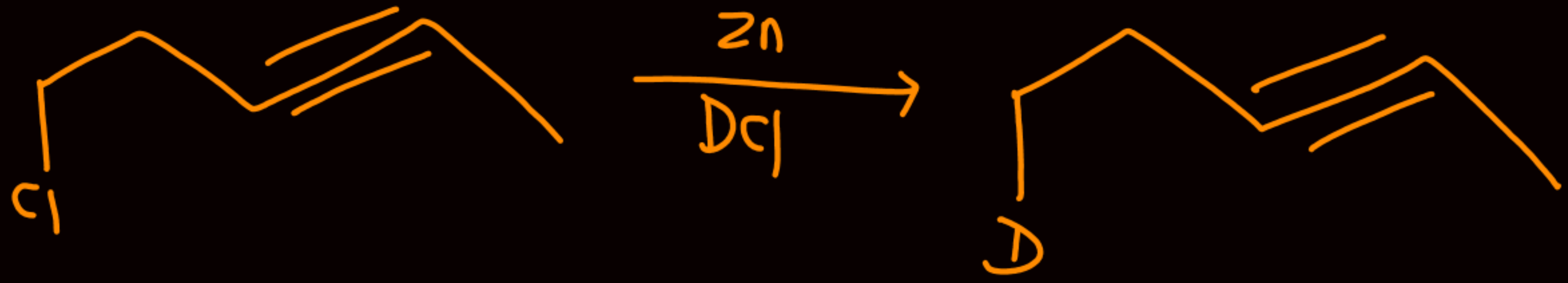
Que



Que



Que



Alkyl Halide ⟶ Alkane

Red P + HI → Highly Reducing agent → किसी भी more En को हटायगा और Hydrogen जोड़ देगा

पड़ोसी ने HI किया और Blush करने लगे
↓
Reduction होगा

Eg

$$CH_3-CH_2-Cl \xrightarrow{Red\,P + HI} CH_3-CH_3$$

$$CH_3-CH(CH_3)-Br \xrightarrow{Red\,P + HI} CH_3-CH_2-CH_3$$

$$CH_3-C(CH_3)_2-Br \xrightarrow{Red\,P + HI} CH_3-CH(CH_3)-CH_3$$

$$CH_3-CH_2-OH \xrightarrow{Red\,P + HI} CH_3-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Red\,P + HI} CH_3-CH_2-CH_3$$

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Red\,P + HI} CH_3-CH_2-CH_3$$

Q $$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[HI]{Red\,P} CH_3-CH_3$$

ALKYL HALIDE → ALKANE

1. Wurtz Reaction
2. Fittig "
3. Wurtz Fittig Reaction
4. Ullman Reaction
5. Frankland Reaction
6. Corey House Reaction

Wurtz -Reaction

(1) 2 mole alkylhalide reacts with 2 mole Na in presence of dryether to form alkane is K/a wurtz Reaction.

$$2R-X + 2Na \xrightarrow{\text{dryether}} R-R + 2NaX$$

$$R-X + 2Na + X-R \xrightarrow{\text{dry ether}} R-R + 2NaX$$

Mechanism

Free Radical Mechanism

$$Na \longrightarrow Na^{+} + e^{-}$$

$$CH_3-Cl + e^{-} \longrightarrow CH_3^{\bullet} + Cl^{\ominus}$$

$$Na \longrightarrow Na^{+} + e^{-}$$

$$CH_3-Cl + e^{-} \longrightarrow CH_3^{\bullet} + Cl^{-}$$

Product $\rightarrow CH_3-CH_3 + 2NaCl$

Ionic Mechanism

$$2Na \longrightarrow 2Na^{+} + 2e^{-}$$

$$CH_3-Cl + 2e^{-} \longrightarrow CH_3^{\ominus} + Cl^{\ominus}$$

$$CH_3^{\ominus} + \overset{\delta+}{CH_3}-\overset{\delta-}{Cl} \longrightarrow CH_3-CH_3 + Cl^{\ominus}$$

Product $\rightarrow CH_3-CH_3 + 2NaCl$

Et – O – Et

Imp points

1. Intermediate → Carbanion & freeradical.
2. k/a Coupling Reaction/ dimerisation Reaction.
3. Product → Higher alkane / Symmetrical alkane is formed.
   ↳ even no of Carbon
4. CH_4 → Never formed
5. Rate of wurtz → R–I > R–Br > R–Cl > R–F
6. dry ether (etherial Solution) → It is used to maintain inert atmosphere in the reaction.
   → It prevents sodium from any reaction (Sodium → Highly Reactive)
   → Moist ether → not taken
   → Sodium reacts with water.
7. Wurtz reaction is suitable to make symmetrical alkane.
   Unsymmetrical alkane → poor yield

Eg → $CH_3-Cl + CH_3-Cl \xrightarrow[\text{ether}]{2Na} CH_3-CH_3 + 2NaCl$

($CH_3^{\bullet}$ from each CH_3-Cl)

$C_2H_5-Cl + C_2H_5-Cl \xrightarrow[Et_2O]{2Na} CH_3-CH_2-CH_2-CH_3 + 2NaCl$

($C_2H_5^{\bullet}$ from each C_2H_5-Cl)

$CH_3-Cl + CH_3-CH_2-Cl \xrightarrow[\text{dry ether}]{2Na} CH_3-CH_2-CH_3$, CH_3-CH_3, $CH_3-CH_2-CH_2-CH_3$

($CH_3^{\bullet}$, $CH_3-CH_2^{\bullet}$)

difficult to separate

Que which product is suitable from wurtz Reaction—

CH_4 —1C→ ✗

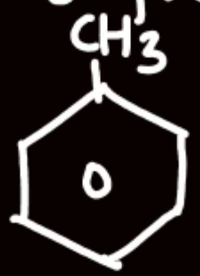
CH_3-CH_3 —2C→ ✓


—3C→ ✗


—4C→ ✓


—5C→ ✗


—6C→ ✓



—7C→ ✗

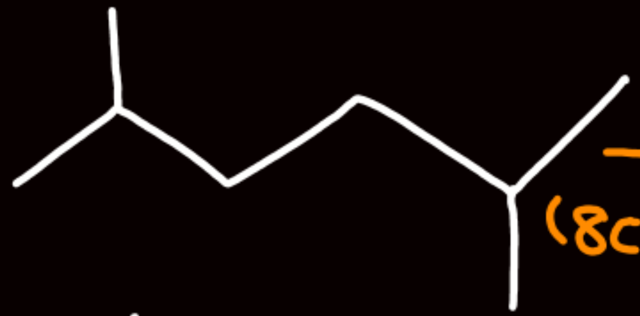


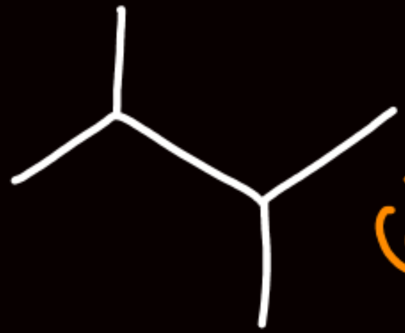
→ ✗

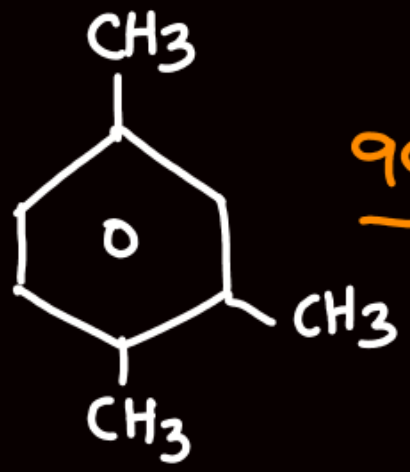
↓

3° alkyl Halide do not give wurtz Reaction product.


→ ✗ (7C)


→ ✓ (8C)


→ ✓ (6C)

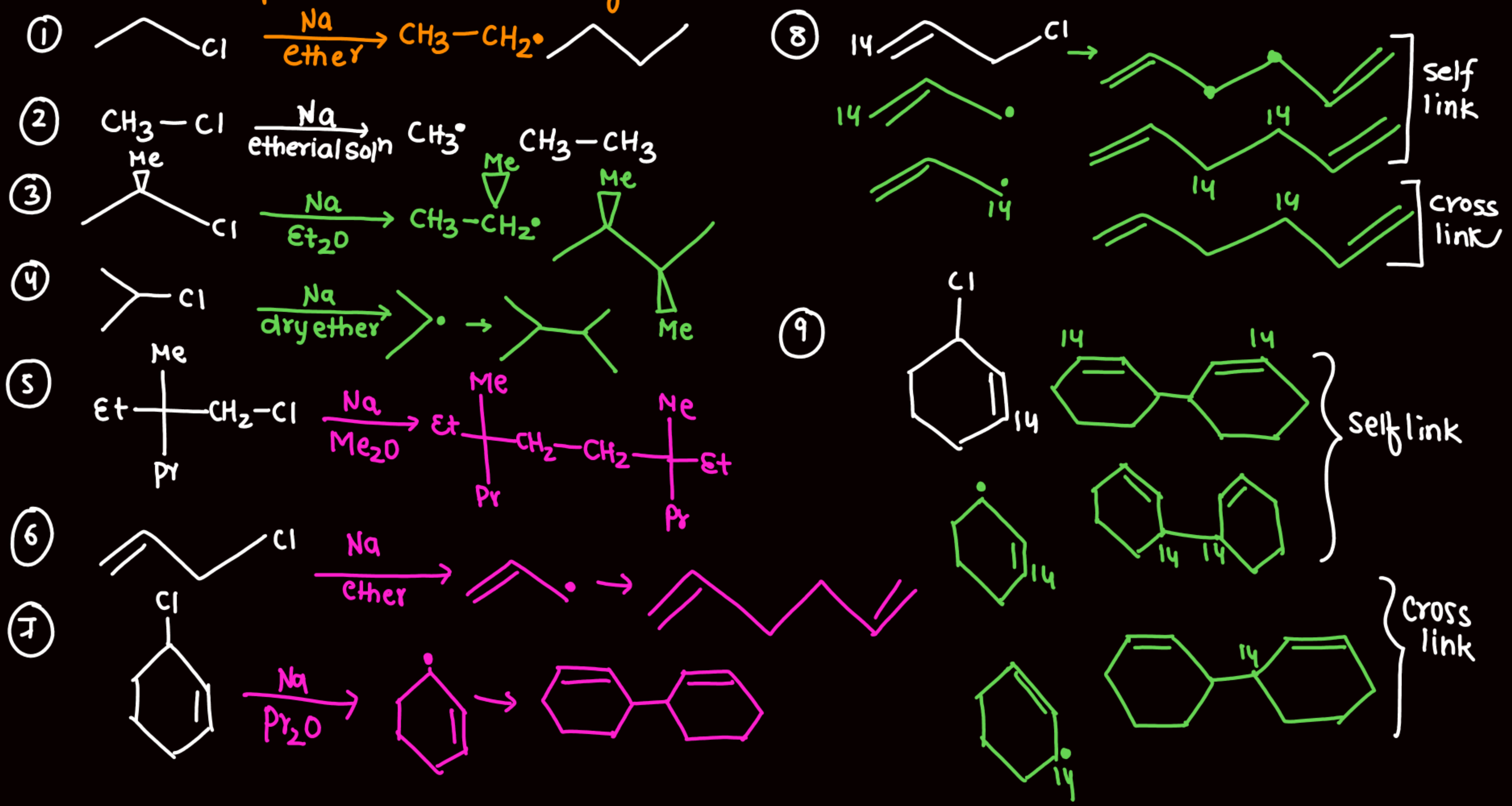


—9C→ ✗

CH_3-OH → ✗

CH_3-O-CH_3 → ✗

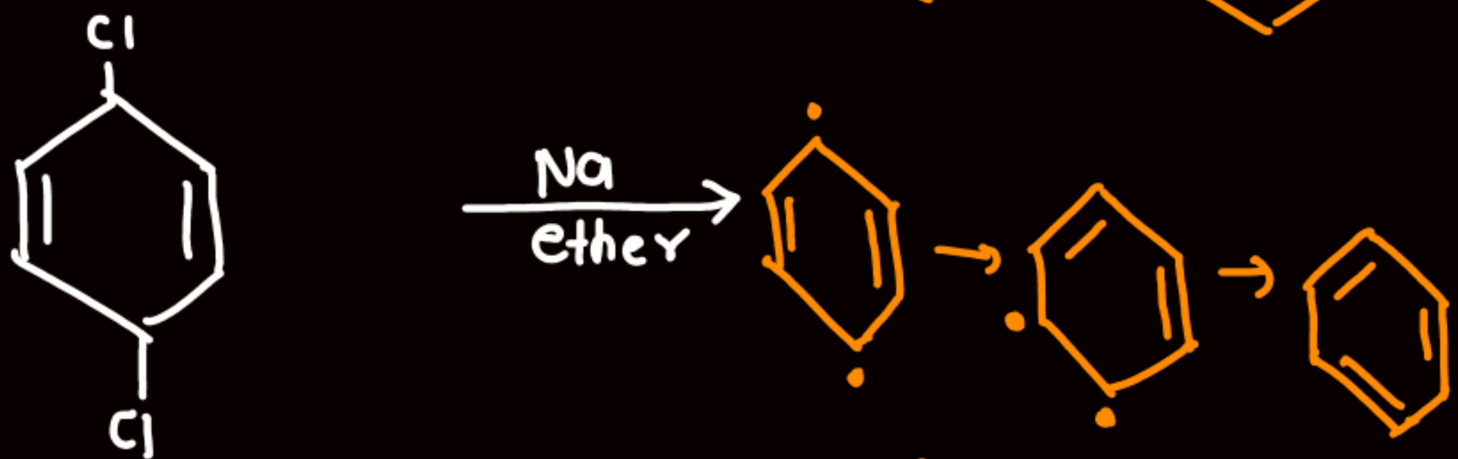
Que write product in the following wurtz Reaction —

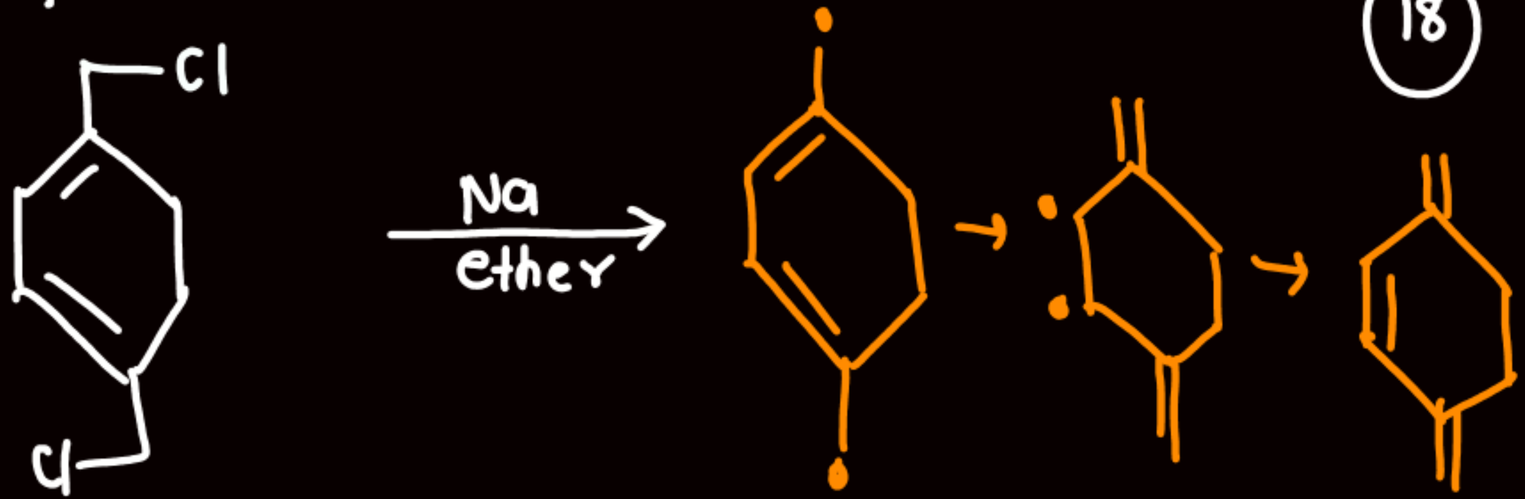


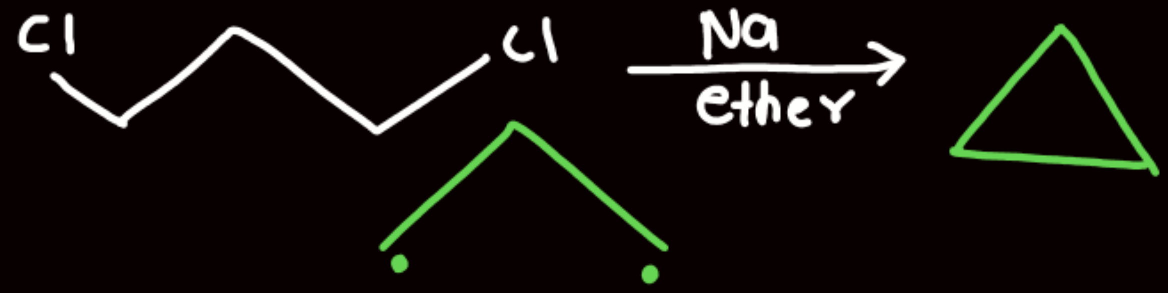
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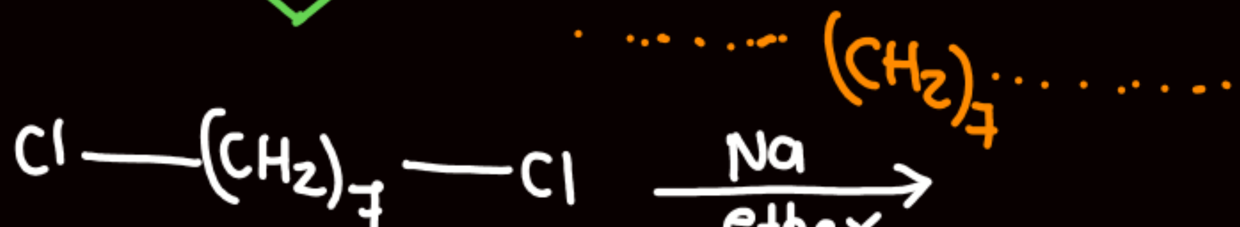

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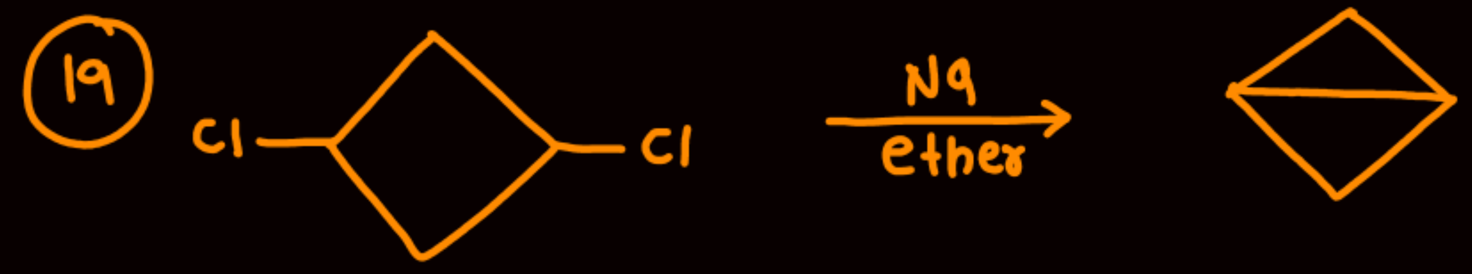
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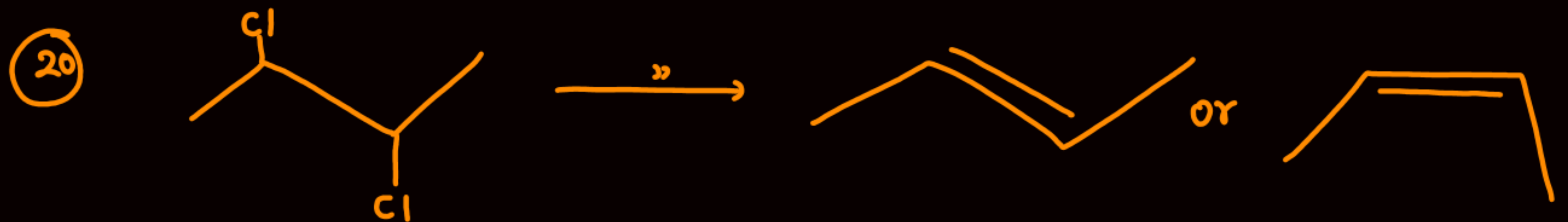
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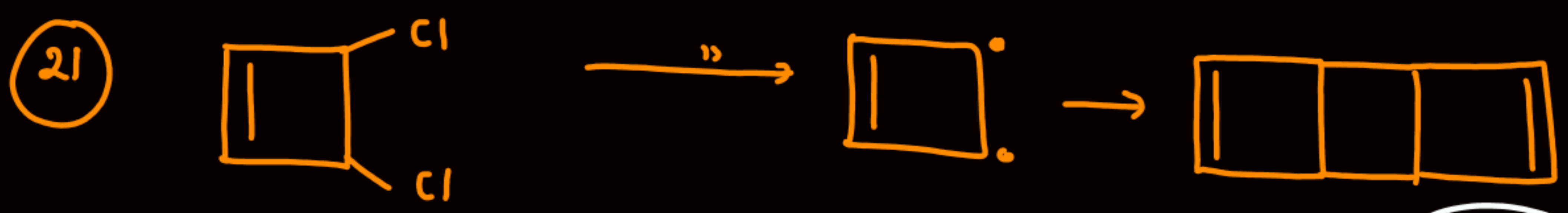

17


18


note → In case of more than 6 Carbon Polymer product is formed.
↳ Ring will not form.

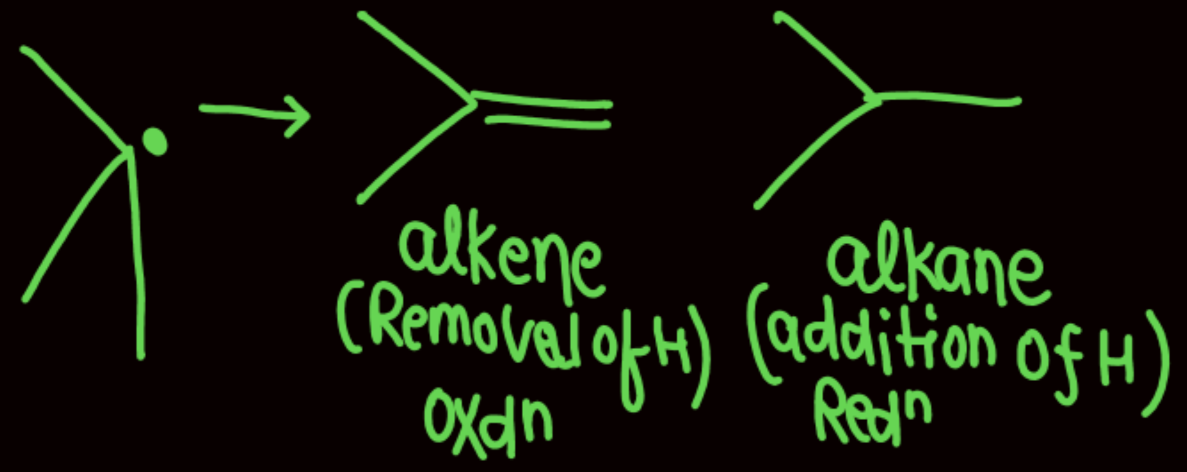








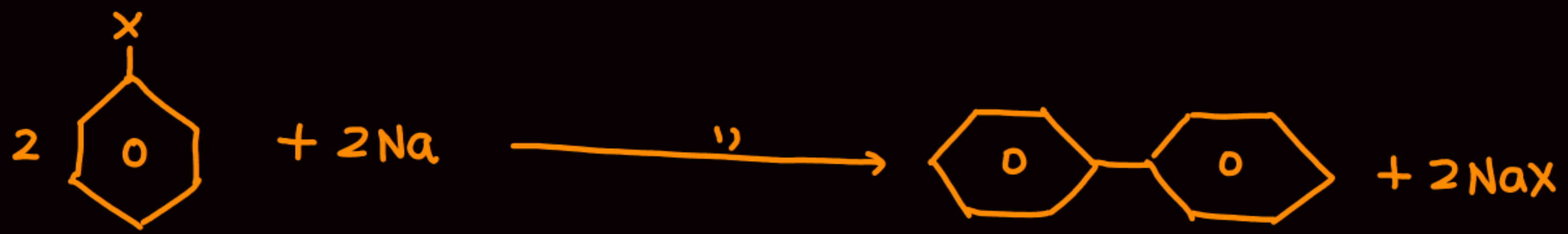
note → 3° degree Free Radical gives disproportionation reaction.



Fittig Reaction

$$2 \text{ mole Aryl Halide} + 2Na \xrightarrow{\text{dry ether}} Ar{-}Ar + 2NaX$$

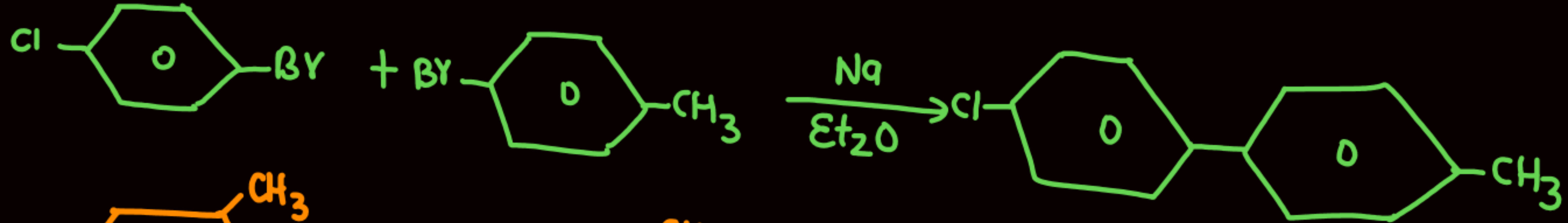
$$2\,Ar{-}X + 2Na \xrightarrow{\text{"}} Ar{-}Ar + 2NaX$$



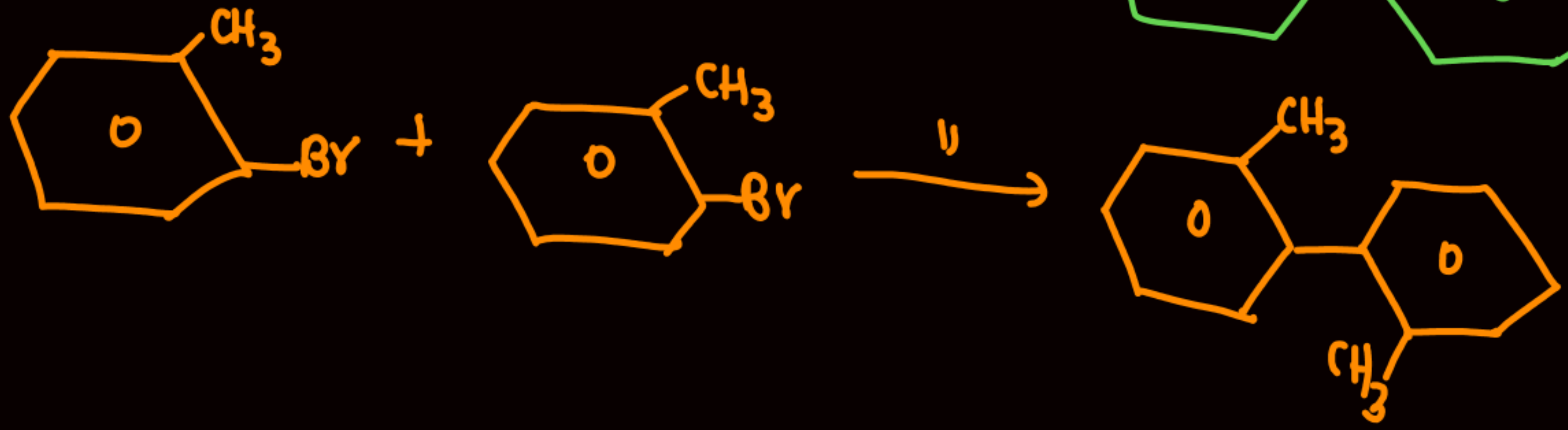
Q.



Q.

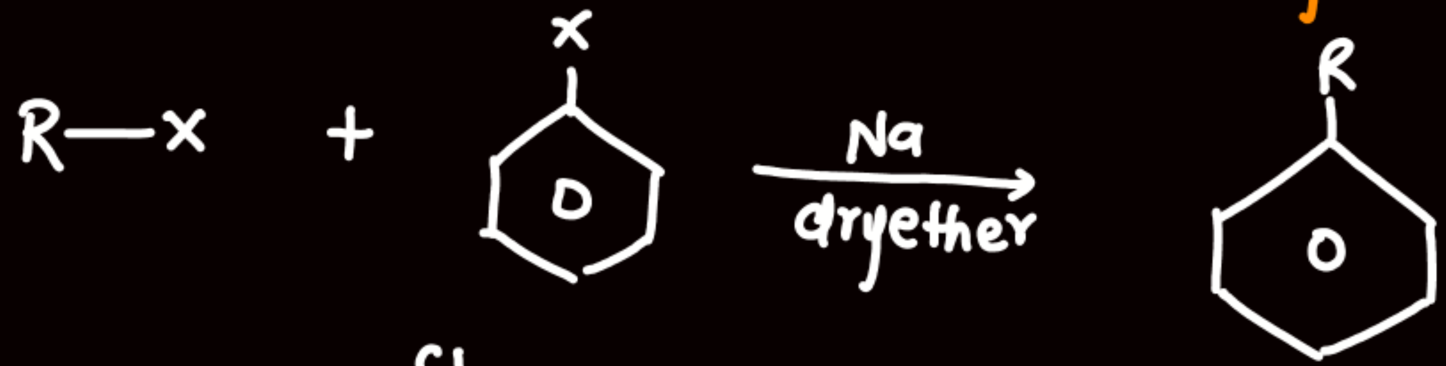


Q.

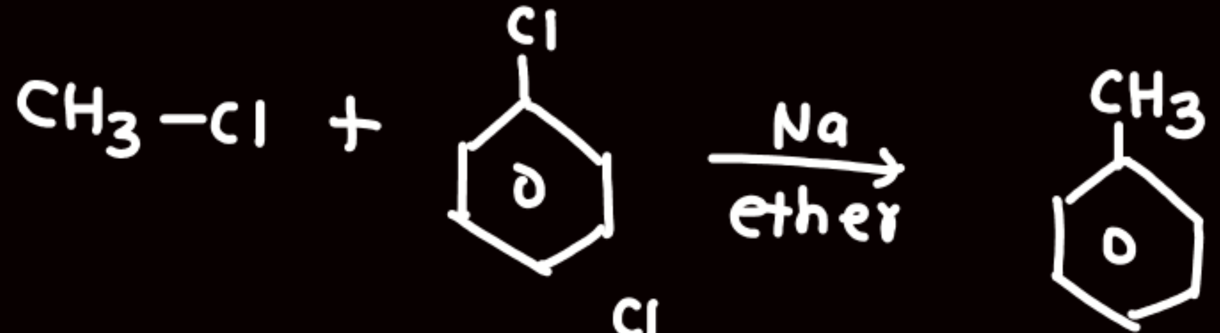


Wurtz-Fittig Reaction

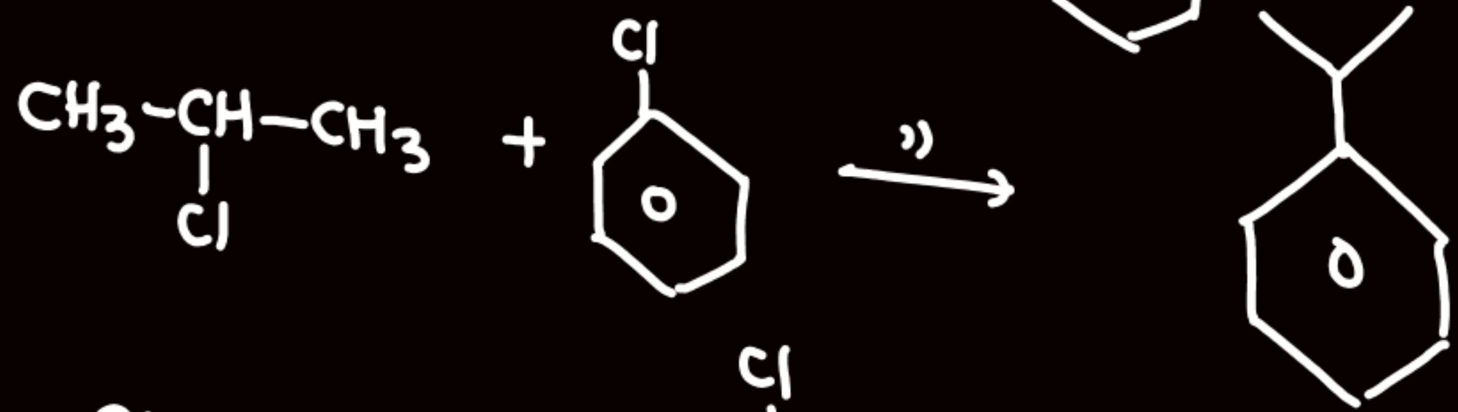




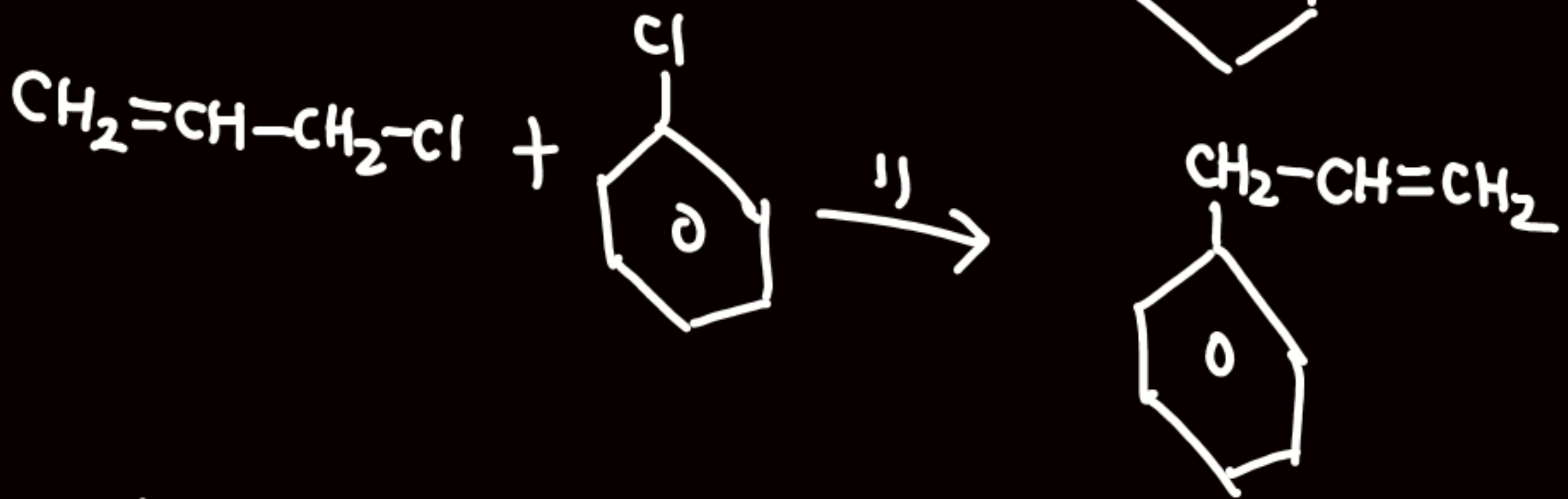
Q



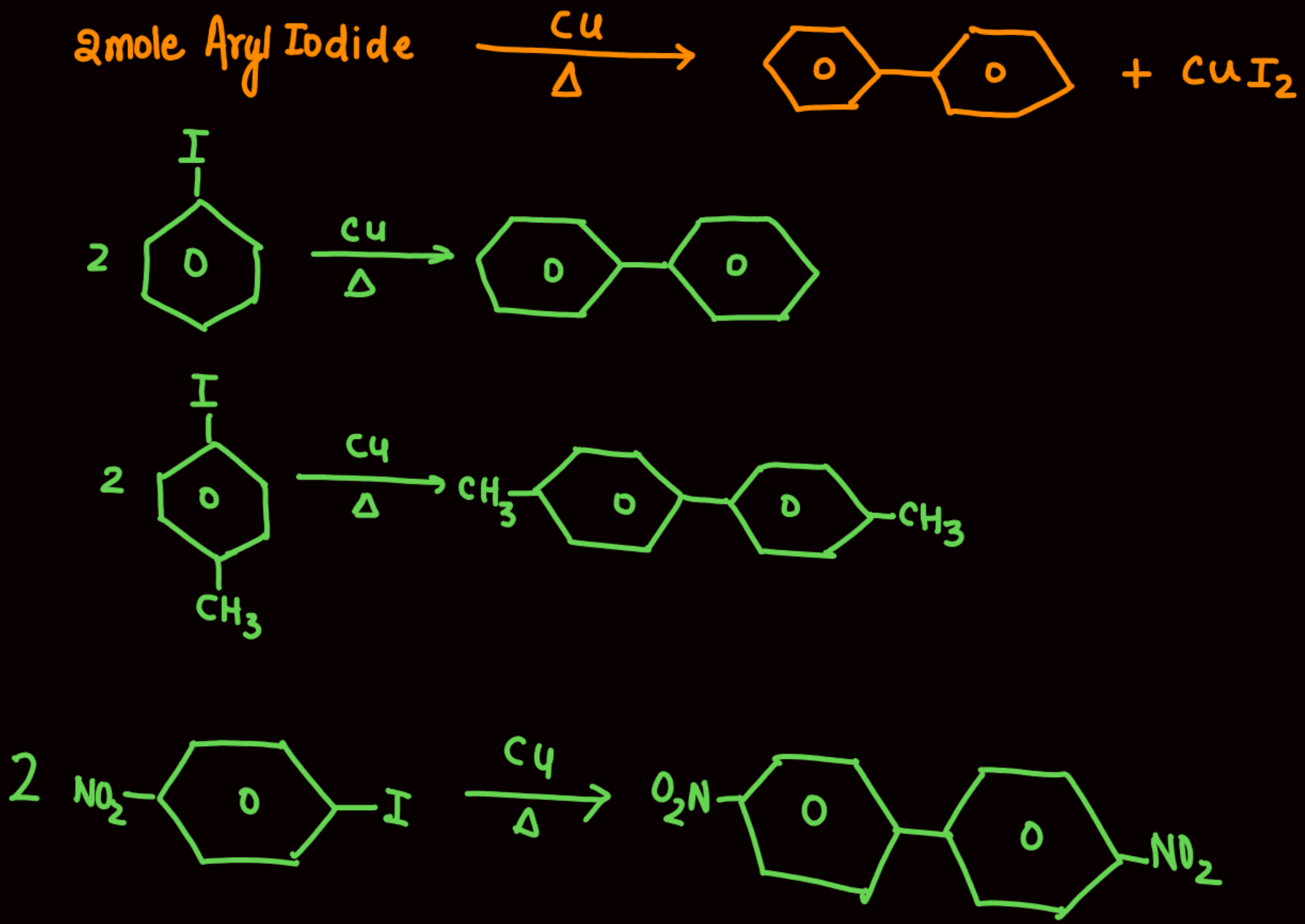
Q



Q



Ullman Reaction



Frankland Reaction

2 mole alkylhalide + 2 Zn $\xrightarrow{\text{dry ether}}$ alkane + ZnX_2

(symmetrical as well as Unsymmetrical alkane is formed in good yield)

$$2R-X \xrightarrow[\text{dry ether}]{2Zn} R-R + ZnX_2$$

mechanism

$$2R-X + 2Zn \longrightarrow 2RZnX$$

$$2RZnX \rightleftharpoons R_2Zn + ZnX_2$$

R_2Zn: dialkylzinc — Frankland Reagent — organometallic Comp → Gives R^- (alkylanion)

$$R_2Zn + R'-X \longrightarrow R-R' + ZnX_2$$

$R_2Zn \rightarrow R^-$ (attacks R')

$R-R'$: alkane

$R = R'$ symm alkane

$R \neq R'$ unsym alkane

Corey House Reaction

Corey House Synthesis

$$R-X \xrightarrow[CuI]{Li} R_2CuLi + R'-X \longrightarrow R-R' + LiX + CuX_2$$

R_2CuLi: dialkyl lithium copper

Gilman Reagent

Organometallic

gives $R^{\ominus}$

Symmetrical as well as Unsymmetrical alkanes both are formed in good yield.

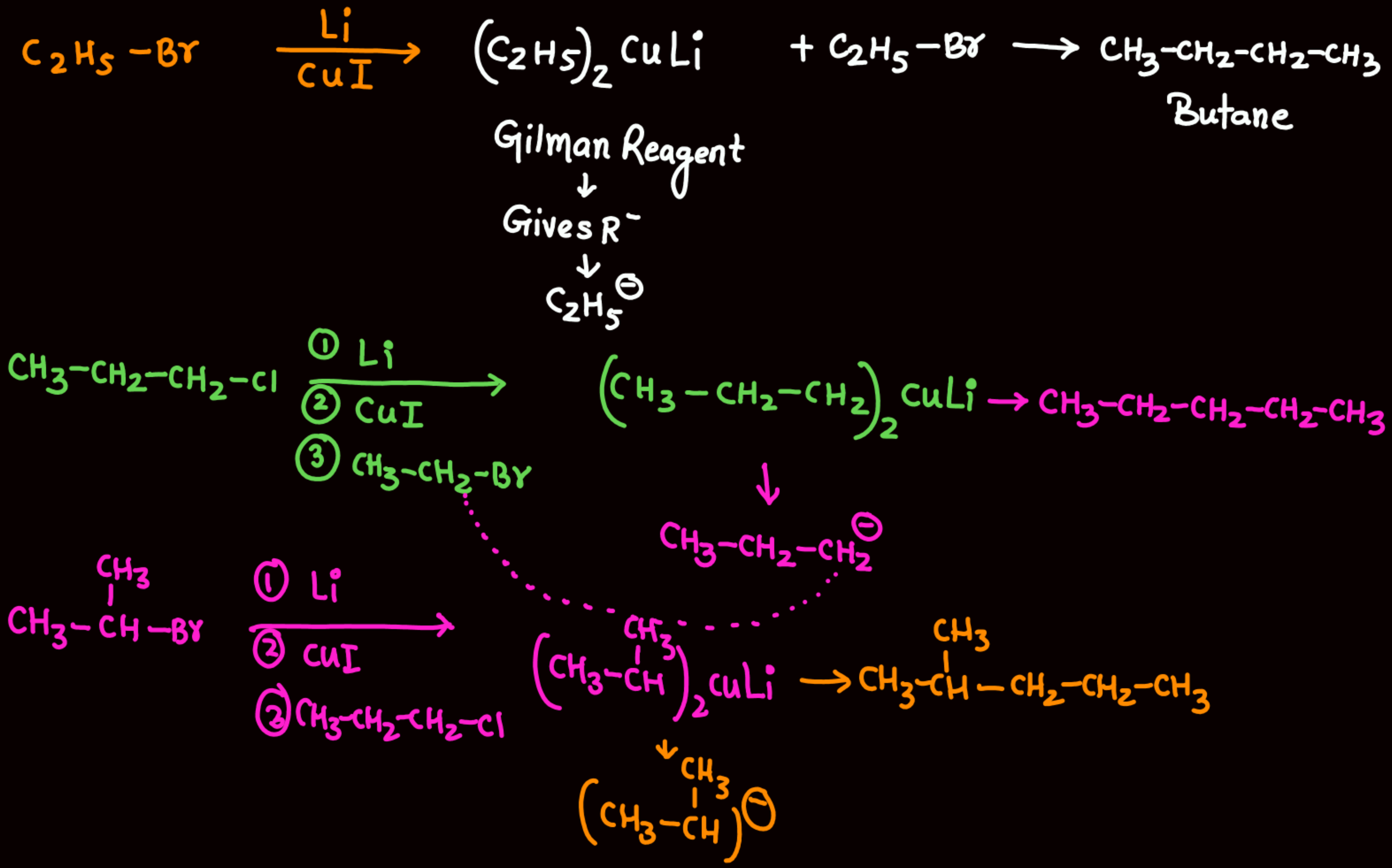
* prefered to make Unsymmetrical alkane.

Q $CH_3I + CH_3CH_2CH_2CH_2I \xrightarrow[CuI]{Li} (CH_3)_2CuLi + CH_3-CH_2-CH_2-CH_2-I$

$(CH_3)_2CuLi \rightarrow CH_3^{\ominus}$

$CH_3-CH_2-CH_2-CH_2-I \rightarrow CH_3-CH_2-CH_2-CH_2-CH_3$

Smaller alkyl Halide forms Gilman Reagent easily.



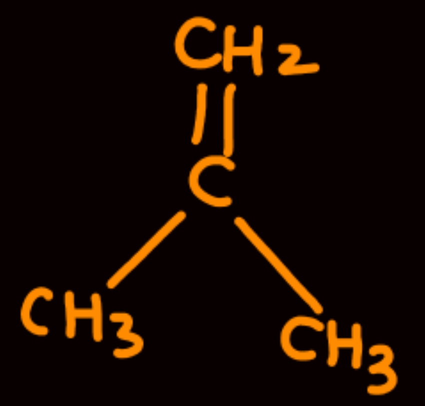
C2H5-Br
Li
CuI
(C2H5)2 CuLi
+ C2H5-Br
CH3-CH2-CH2-CH3
Butane
Gilman Reagent
Gives R-
C2H5
CH3-CH2-CH2-Cl
① Li
② CuI
③ CH3-CH2-BY
(CH3-CH2-CH2)2 CuLi
CH3-CH2-CH2-CH2-CH3
CH3-CH2-CH2
CH3
CH3-CH-BY
① Li
② CuI
③ CH3-CH2-CH2-Cl
CH3
(CH3-CH)2 CuLi
CH3
CH3-CH-CH2-CH2-CH3
CH3
(CH3-CH)

$$CH_3-Cl + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl \xrightarrow[\text{② CuI}]{\text{① Li}} (CH_3)_2CuLi$$

3° alkyl Halide

note 3° alkyl halide gives alkene product.

↓



$+ CH_4 + LiCl + CuCl_2$

(Remove H^+)

Method of Preparation of Alkane

1. Unsaturated Hydrocarbon
2. alkylhalide
3. aldehyde/ketone ⟶ alkane
   - (1) Wolf Kishner Reaction
   - (2) Clemensen Reaction
4. Carboxylic acid ⟶ alkane
   - Soda lime decarboxylation
   - kolbe electrolysis
5. Grignard
6. alcohol/aldehyde/ketone/carboxylic acid or its derivative →

Clemmenson Reduction Reaction

$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[HCl]{Zn-Hg} CH_3-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[HCl]{Zn-Hg} CH_3-CH_2-CH_3$$

(Zn-Hg → zn amalgum)

Clemenson का जंग होगा जिसमें acid attack होगा → oxygen जल जाएगा उसकी जगह पर Hydrogen लग जाएगा।

* This is a reduction reaction in acidic medium.

Wolf Kishner Reduction Reaction

$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[KOH]{NH_2-NH_2} CH_3-CH_3$$

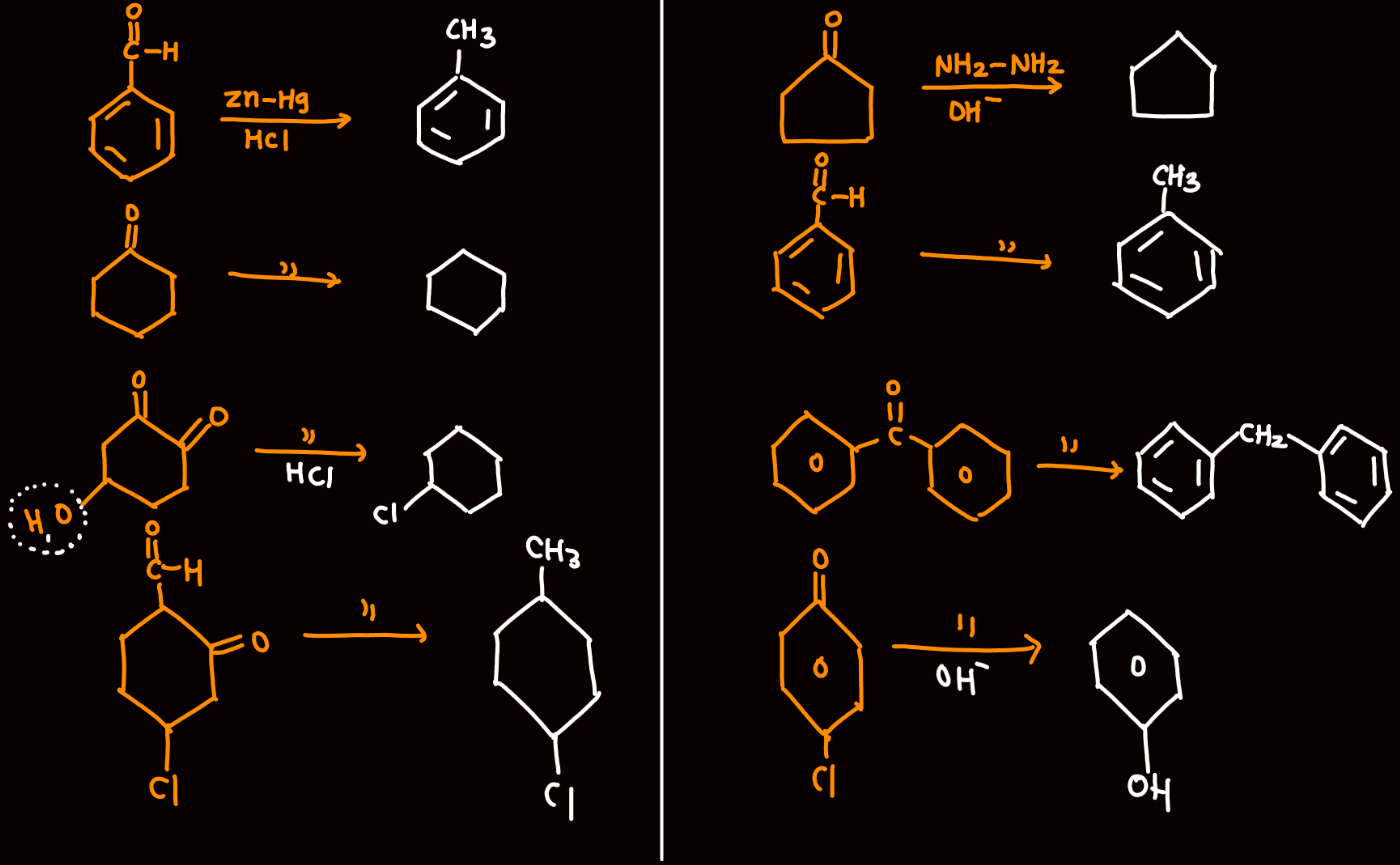
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[KOH]{NH_2-NH_2} CH_3-CH_2-CH_3$$

(aldehyde/ketone)

A/K → Hygine Maintain → Vanity Bus

Hygine ↓ Hydrazine; Bus ↓ Base

* This is a reduction reaction in basic medium.



Zn-Hg
HCl
NH2-NH2
OH⁻
CH3
C-H
"
HCl
Cl
HO
CH2
OH

Soda-Lime decarboxylation

Caustic Soda ($NaOH$) & Quick Lime (CaO) → Removal of CO_2

- 3:1 ratio of soda & lime is taken & CO_2 is removed to form alkane.

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{NaOH + CaO} CH_4$$

ethanoic acid → Methane

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{NaOH + CaO} R-\overset{O}{\overset{\|}{C}}-\bar{O}\,Na^+ \longrightarrow R^{\ominus} + CO_2 \xrightarrow[\text{from Solvent}]{H} R-H + CO_2$$

or $R-\overset{O}{\overset{\|}{C}}-\bar{O}\,K^+$ (Na_2CO_3)

① Carbanion intermediate.

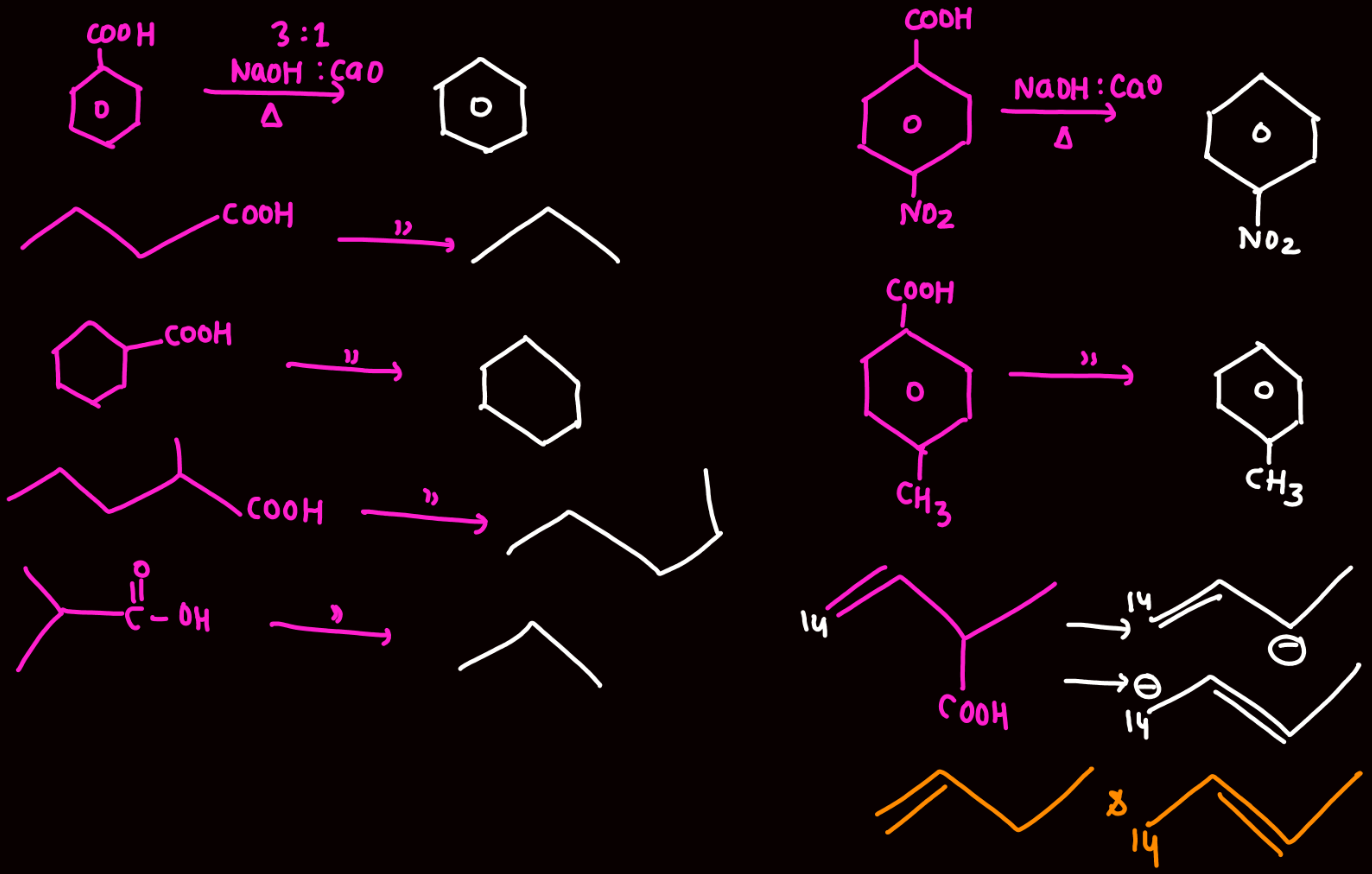
② Step down Reaction → product has one Carbon lesser.

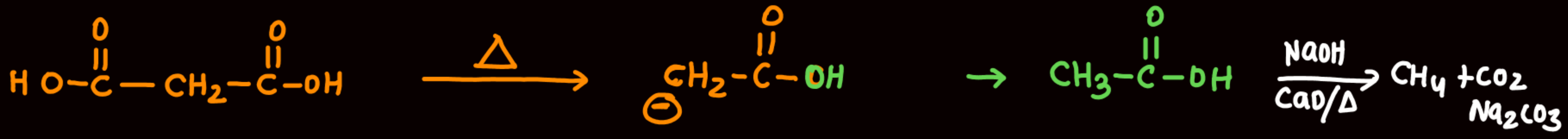
③ CH_4 methane is formed. ④ Rate of decarboxylation ∝ Stab of intermediate

$$H-\overset{O}{\overset{\|}{C}}-\bar{O}\,Na^+ \xrightarrow[\Delta]{NaOH + CaO} H_2 + CO_2$$

⑤ Released CO_2 forms Na_2CO_3.

$$CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\,Na^+ \xrightarrow[\Delta]{NaOH + CaO} CH_4 + CO_2$$


COOH
3 : 1
NaOH : CaO
Δ
COOH
"
COOH
"
COOH
"
O
C – OH
"
COOH
NaOH : CaO
Δ
NO2
NO2
COOH
"
CH3
CH3
14
COOH
14
14
&
14

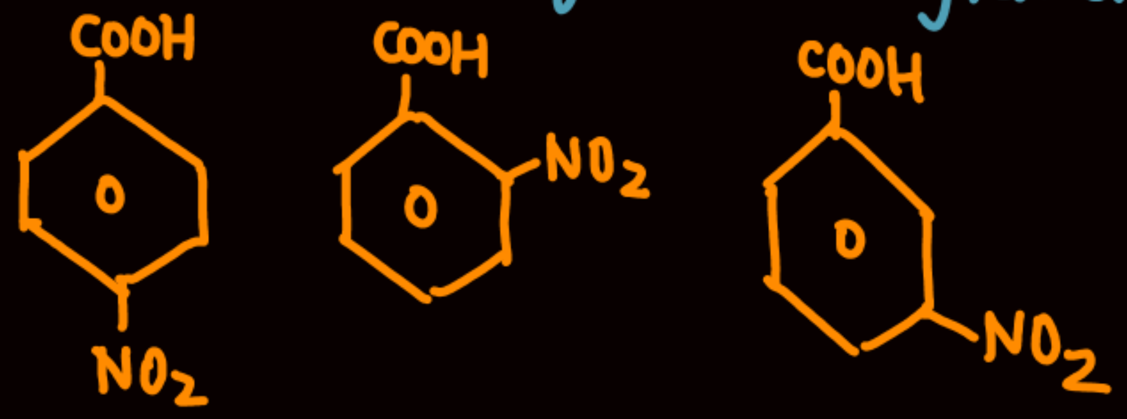


Dicarboxylic acid ↓ we don't need (NaOH + CaO)/Δ

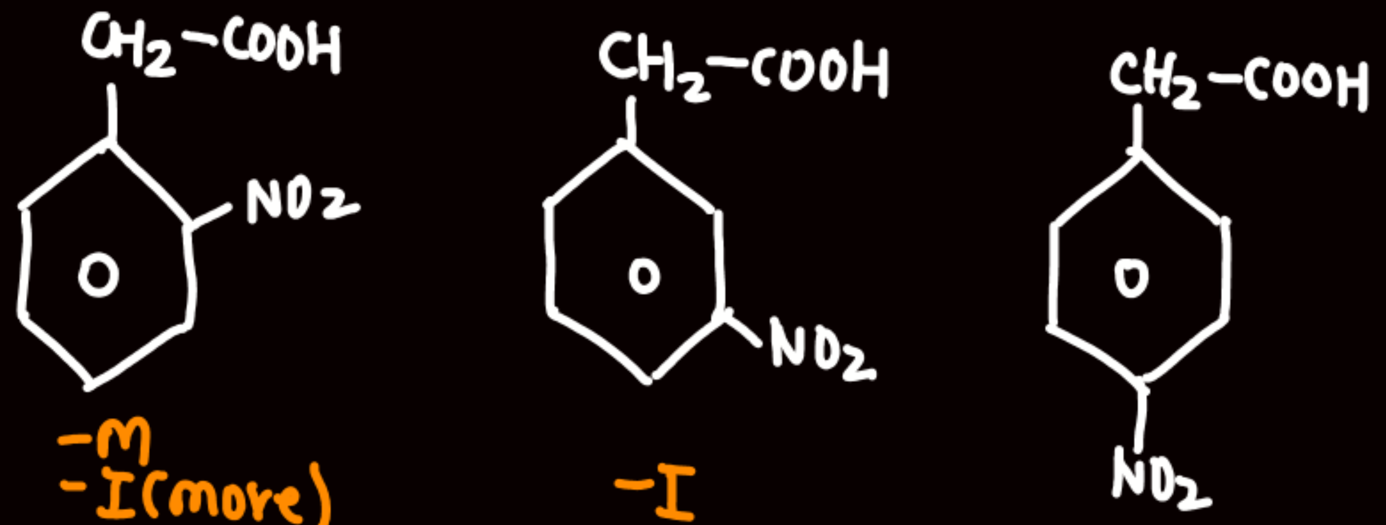
Carbanion intermediate is Resonance Stabilised.

Monocarboxylic acid

Que Compare of rate of decarboxylation–



Ans → b > c > a — I order

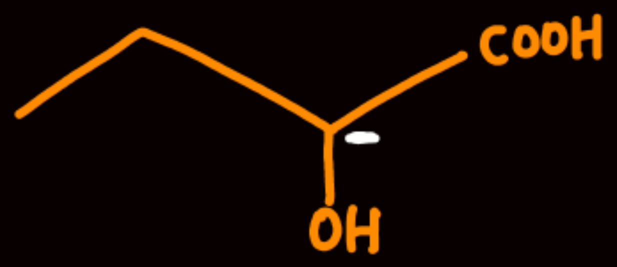


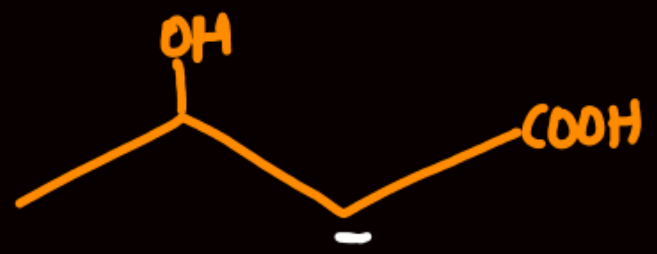
–M
–I (more)

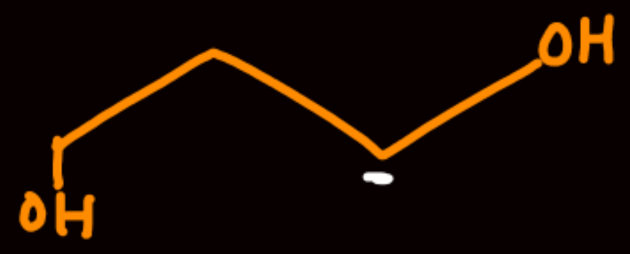
–I

–M
–I (less)

a > c > b





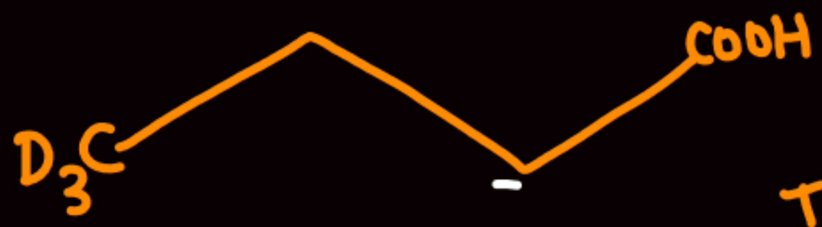


a > b > c





a > b > c > d





Kolbe's electrolysis

$$\begin{matrix} R-\overset{O}{\overset{\|}{C}}-O^{-}\ Na^{+} & OH-H \\ R-\underset{O}{\underset{\|}{C}}-O^{-}\ Na^{+} & OH-H \end{matrix} \xrightarrow{\text{electrolysis}} \underset{\text{alkane}}{R-R} + 2CO_2 + 2NaOH + H_2$$

(R—R + 2CO₂: anode; 2NaOH + H₂: cathode)

- 2 mole Salt of Carboxylic acid $\xrightarrow{\text{electrolysis}}$ alkane + 2CO₂ + 2NaOH + H₂
- anode → CO_2 gas

  Cathode → H_2 gas
- Final solution will be basic (NaOH formed)
- Free Radical intermediate.

$R^{\bullet}$ $R-\overset{O}{\overset{\|}{C}}-O^{-}Na^{+}$ OH—H

$R'^{\bullet}$ $R'-\overset{O}{\overset{\|}{C}}-O^{-}Na^{+}$ OH—H $\xrightarrow{\text{electrolysis}}$ $R-R + R'-R' + R-R' + 2CO_2 + 2NaOH + H_2$

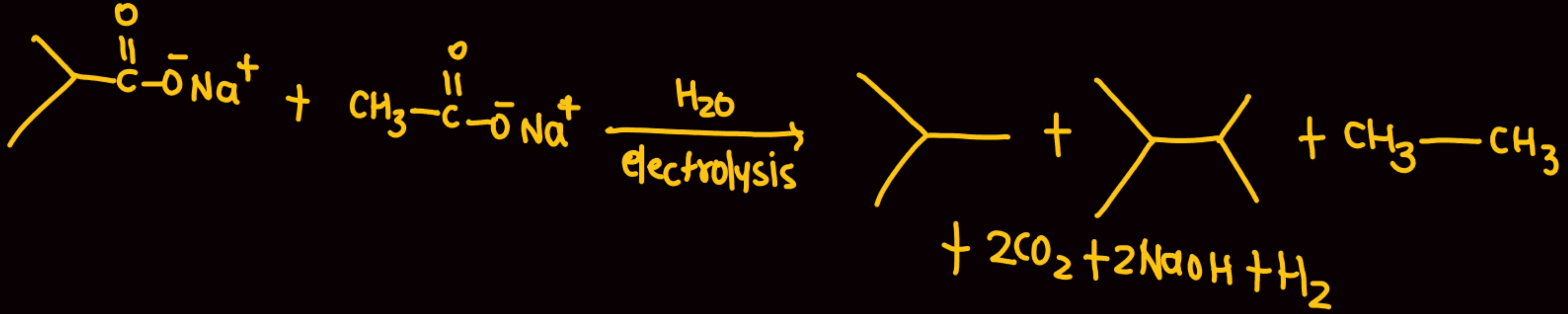
Que $2\ CH_3-CH_2-\overset{O}{\overset{\|}{C}}-\bar{O}\ Na^+ \xrightarrow[\text{electrolysis}]{H_2O} \underbrace{CH_3-CH_2-CH_2-CH_3 + 2CO_2}_{\text{anode}} + \underbrace{2NaOH + H_2}_{\text{Cathode}}$

Que $2\ H-\overset{O}{\overset{\|}{C}}-\bar{O}\ Na^+ \xrightarrow[\text{electrolysis}]{H_2O} H_2 + 2CO_2 + 2NaOH + H_2$

Que



Que



Grignard

$R{-}X \xrightarrow[\text{ether}]{Mg} RMgX$

alkyl halide → Grignard

Organometallic

↓

R^-

(alkyl anion)

$RMgX \xrightarrow{R'{-}X} R{-}R'$ alkane

$RMgX \xrightarrow[H_3PO_4,\ H_2SO_4]{H_2O,\ HCl,\ HNO_3} R{-}H$ alkane

$R{-}X \xrightarrow[\text{ether}]{Na}$ W.R

$R{-}X \xrightarrow[\text{ether}]{Mg}$ Grignard

$R{-}X \xrightarrow[\text{ether}]{Zn}$ F.R

$Ar{-}X \xrightarrow[\text{ether}]{Na}$ Fittig

$R{-}X + Ar{-}X \xrightarrow{\text{''}}$ W.F.R

$Ar{-}I \xrightarrow[\Delta]{Cu}$ U.R

$R{-}X \xrightarrow[CuI]{Li} \xrightarrow{R'{-}X} R{-}R'$ C.H.S.R

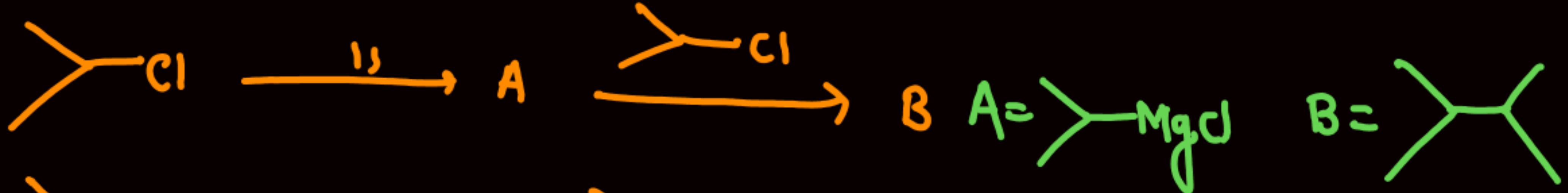
Que $CH_3{-}Cl \xrightarrow[\text{ether}]{Mg} A \xrightarrow{HCl} B$

$A = CH_3MgCl$ $B = CH_4$

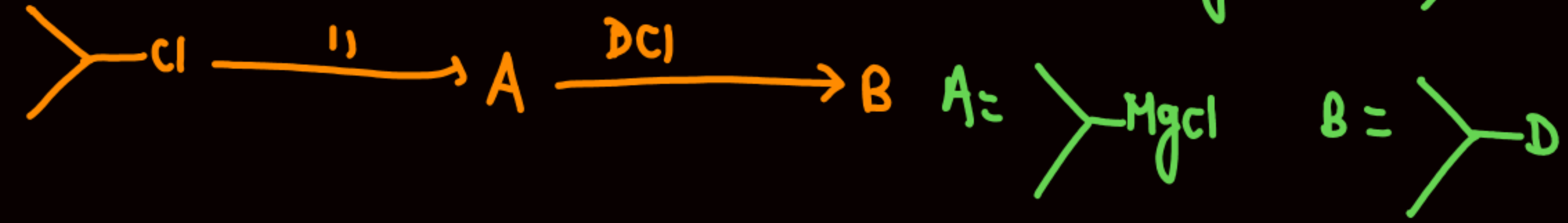
Que $CH_3{-}\underset{}{\overset{CH_3}{CH}}{-}Br \xrightarrow{\text{''}} A \xrightarrow{CH_3{-}Cl} B$

$A = CH_3{-}\overset{CH_3}{CH}{-}MgBr$ $B = CH_3{-}\overset{CH_3}{CH}{-}CH_3$

Que



Que



Que

$\overset{R^-}{RMgX}$ + H—OH ⟶ R—H

+ H—NH_2 ⟶ R—H

+ H—NH—C(=O)—R ⟶ R—H

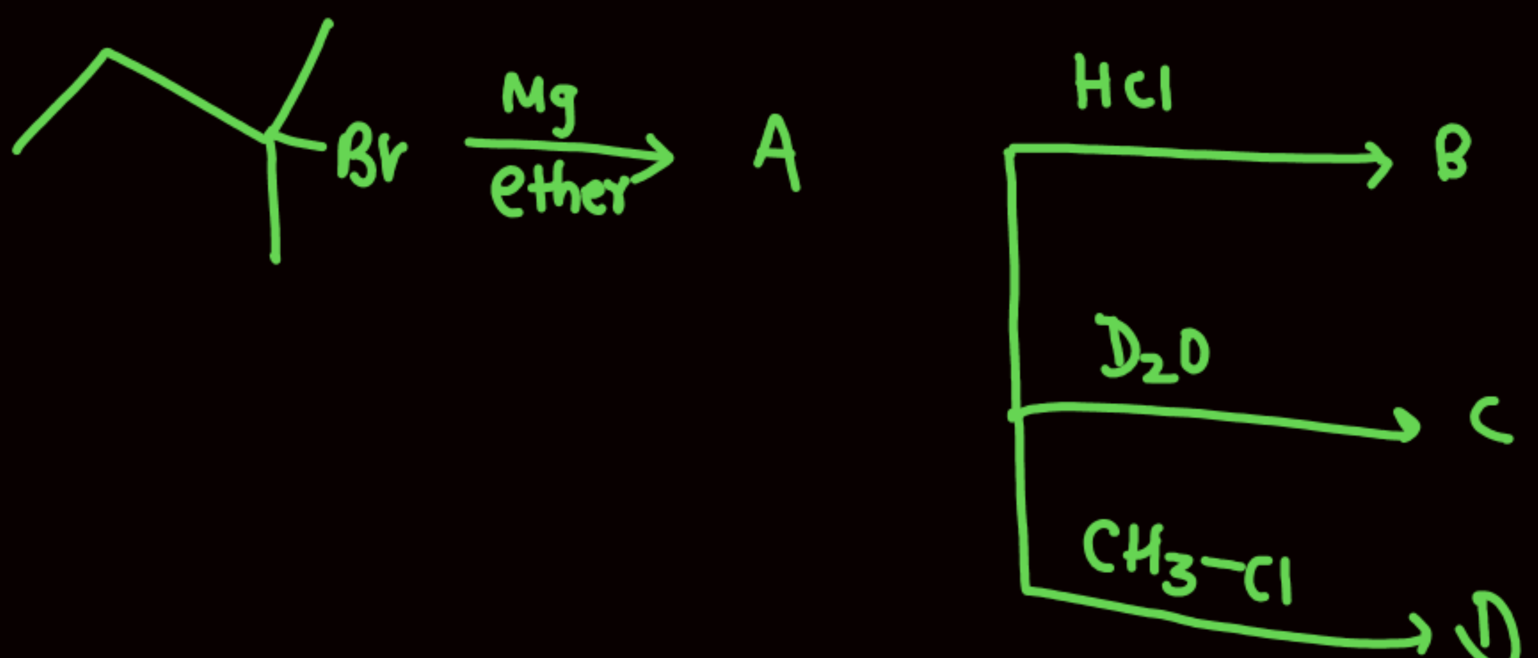
+ H—OR ⟶ R—H

+ H—O—C(=O)—R ⟶ R—H

+ H—CH(—C(=O)—R)(—C(=O)—R) ⟶ R—H

+ H—C≡C—R ⟶ R—H

Que



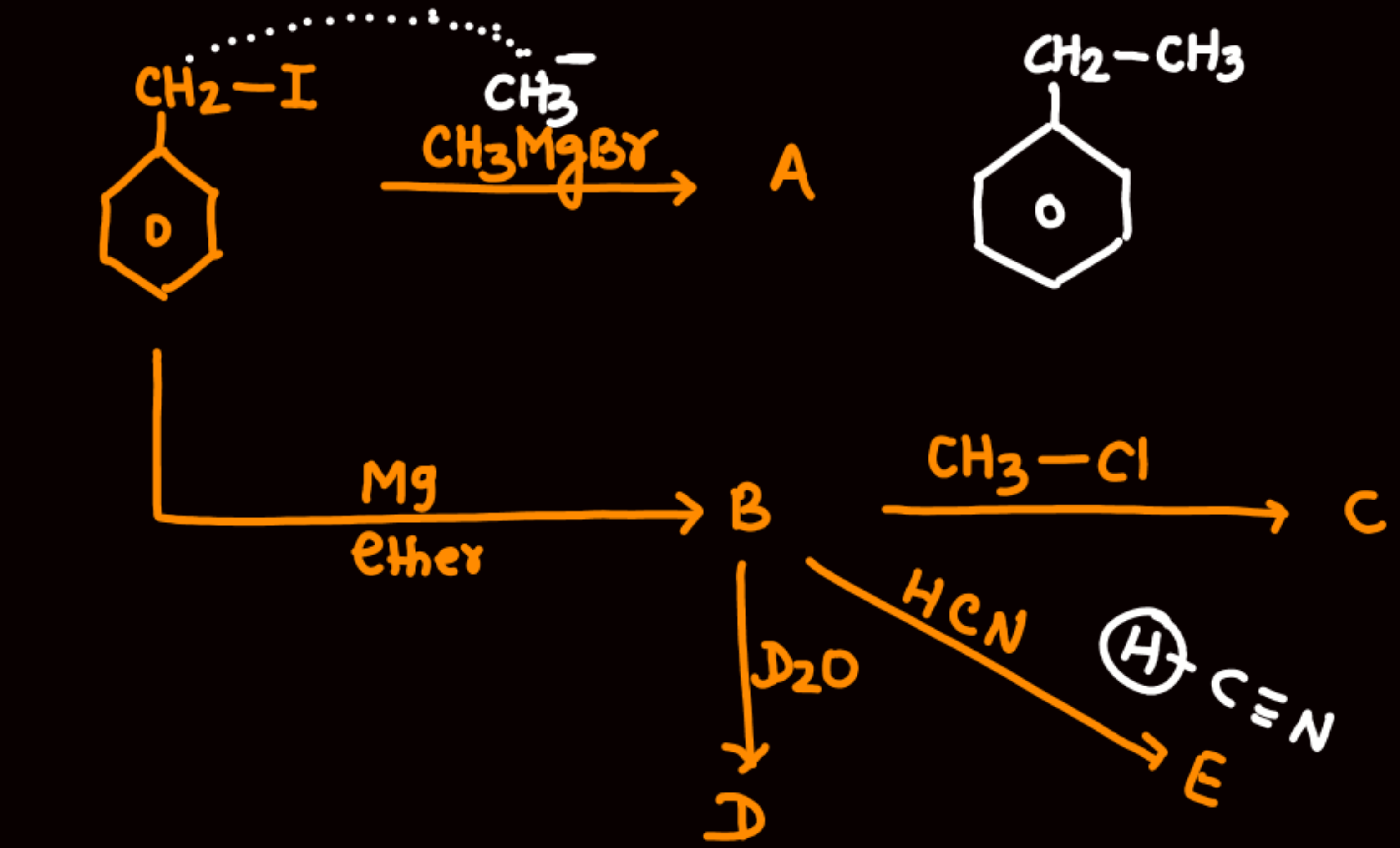
(A)

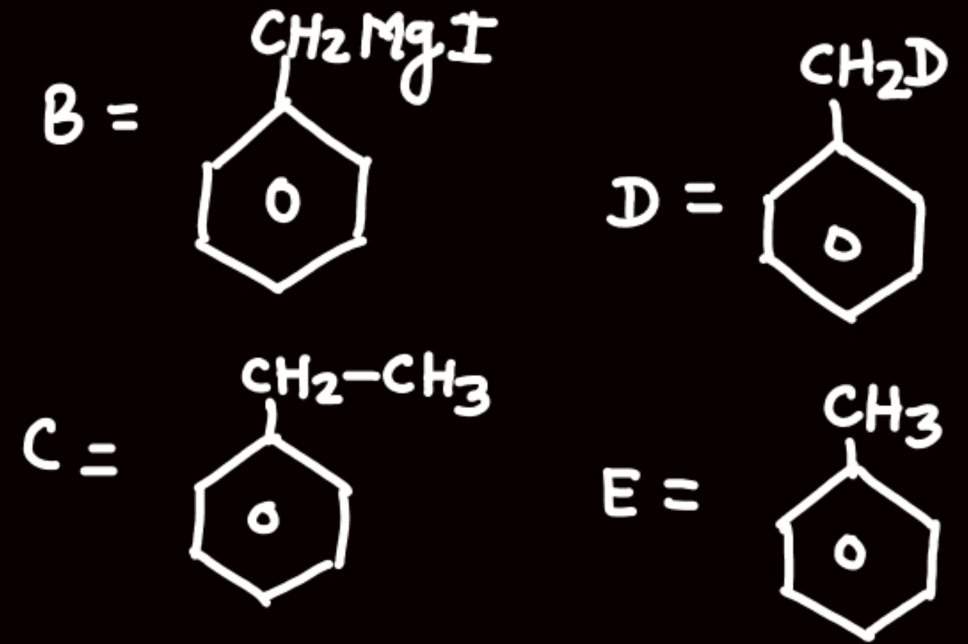

(B)


(C)

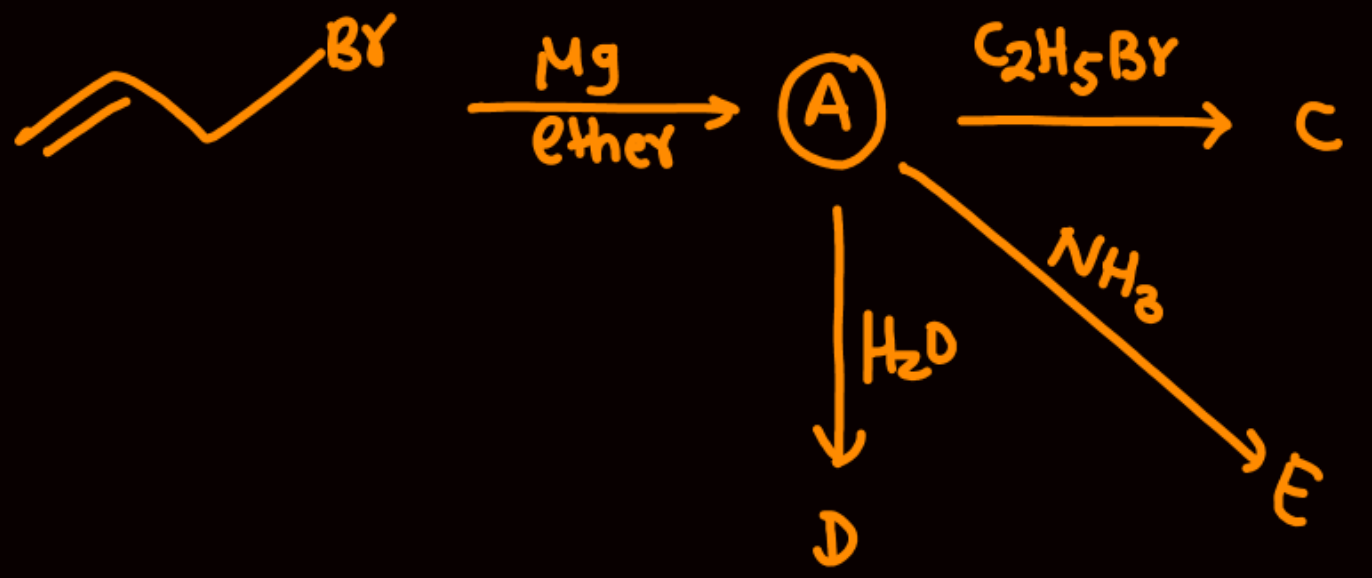

(D)

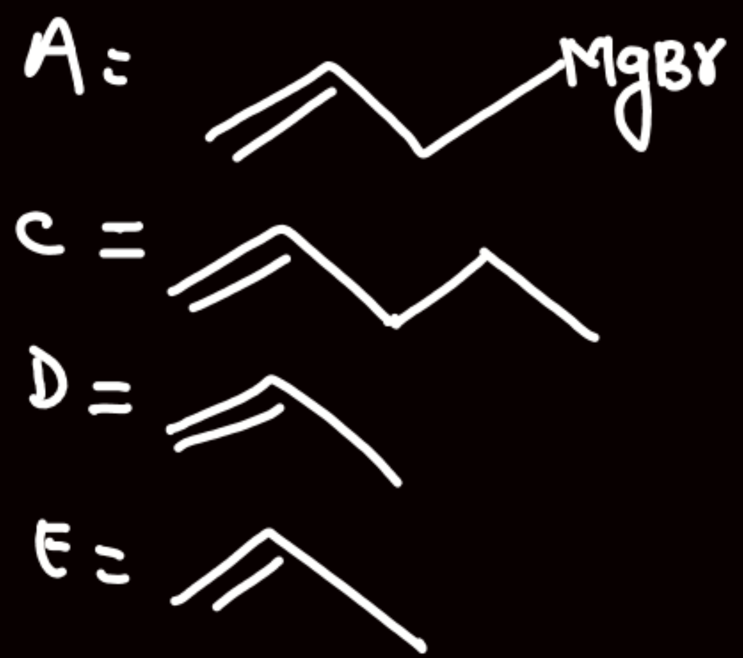

Q

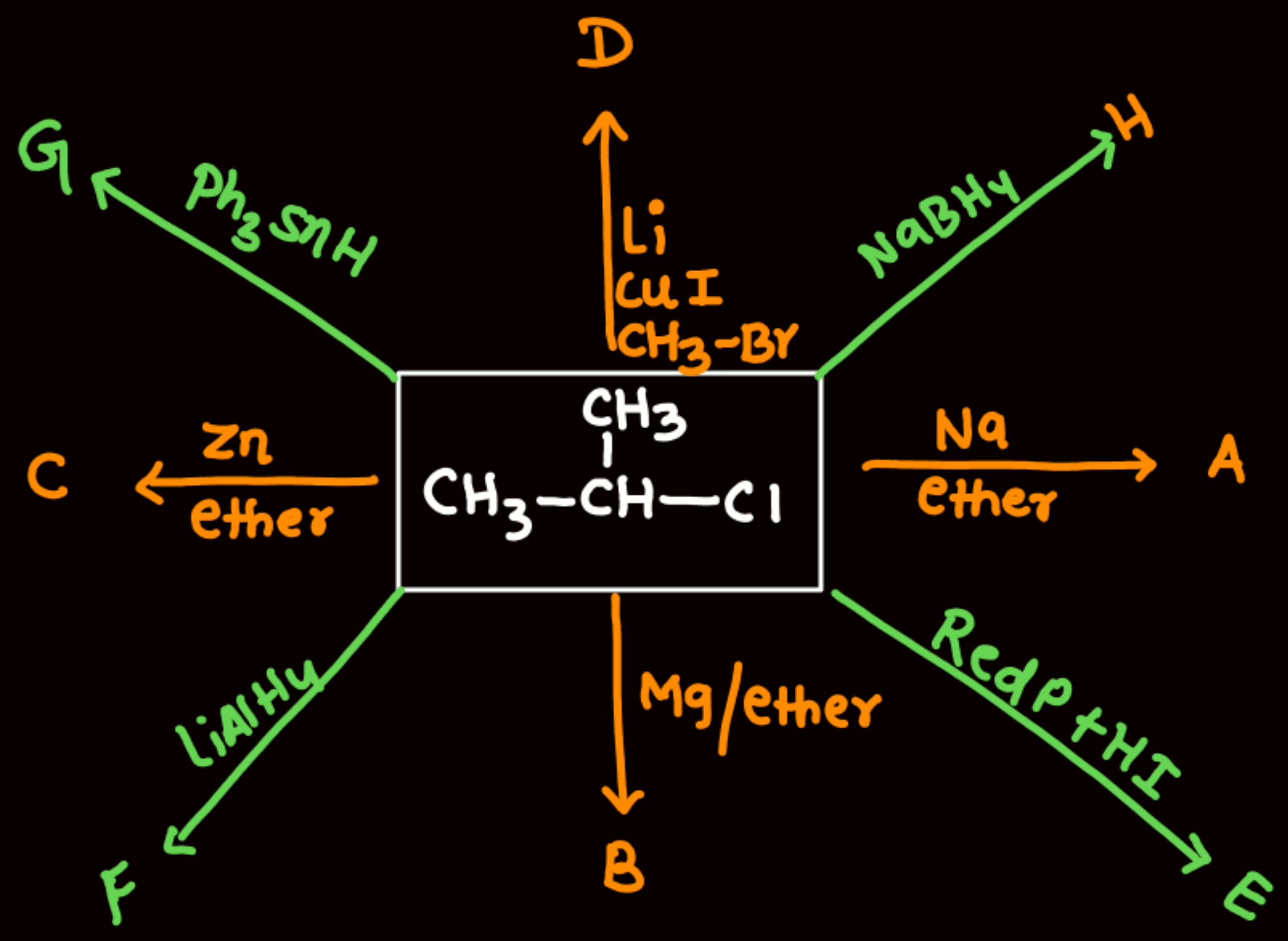

CH2—I
CH3
CH3MgBr
A
CH2—CH3
Mg
ether
B
CH3—Cl
C
D2O
D
HCN
H—C≡N
E


B =
CH2MgI
D =
CH2D
C =
CH2—CH3
E =
CH3

Q


Br
Mg
ether
A
C2H5Br
C
H2O
D
NH3
E


A :
MgBr
C =
D =
E =



$A = CH_3-CH(CH_3)-CH(CH_3)-CH_3$

$B = CH_3-CH(CH_3)-MgCl$

$C = (CH_3-CH(CH_3))_2Zn \rightarrow CH_3-CH(CH_3)-CH(CH_3)-CH_3$

$D = (CH_3-CH(CH_3))_2CuLi \rightarrow CH_3-CH(CH_3)-CH_3$

$E = CH_3-CH_2-CH_3$

$F = CH_3-CH_2-CH_3$

$G = CH_3-CH_2-CH_3$

$H = CH_3-CH_2-CH_3$

Red P + HI Reduction Reaction

Red Padosi ने HI किया
More En Bye Bye हो जाएगा

→ Removes more En atom & add Hydrogen.

$$CH_3-Cl \xrightarrow{Red P + HI} CH_4$$

$$CH_3-OH \xrightarrow{\text{"}} CH_4$$

$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{"}} CH_3-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{"}} CH_3-CH_2-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{"}} CH_3-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{\text{"}} CH_3-CH_3 + CH_3-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\text{"}} CH_3-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{\text{"}} CH_3-CH_3$$

Physical properties of Alkane

① • Alkanes are inert in nature. ($C—C$ bond & $C—H$ bond) → donot break easily at room temp.
- ↳ Unreactive nature
  - ↳ Paraffin
- $C—C$ bond: Strong bond
- $C—H$ bond: Strong bond

② • Alkanes are nonpolar. ($C—C$ bond & $C—H$ bond) → nonpolar
- $C—C$ bond: $\Delta En = 0$
- $C—H$ (C = 2.5, H = 2.1): $\Delta En = 0.4$

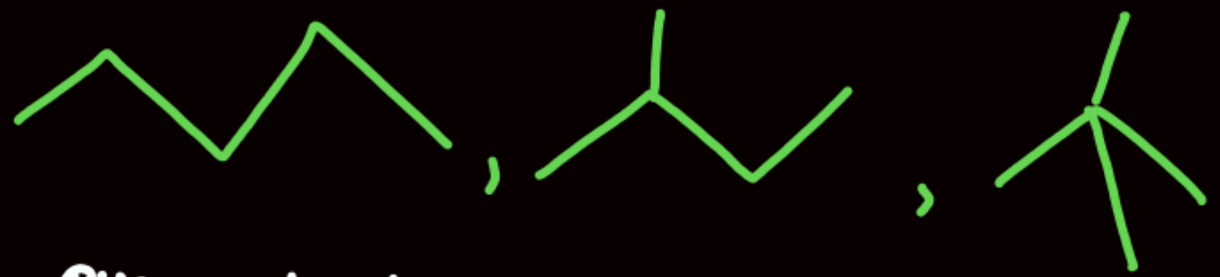
③ • Alkanes are soluble in nonpolar solvent eg Benzene C_6H_6, CS_2, CCl_4 etc.

④ • Boiling point ∝ Num of carbon

Boiling point ∝ $\dfrac{1}{\text{Branching}}$



(B.P.)



(a>b>c)

⑤ • Melting Point → alkanes having even Carbon have more Melting Point than alkanes having odd carbon. → even Carbon has more packing efficiency.

CH_3-CH_3 > $CH_3-CH_2-CH_3$ (MP)



(MP)

Chemical Reactions of Alkane

1. Substitution Reaction
   - photohalogenation
     - Fluorination
     - Chlorination
     - Bromination
     - Iodination
   - Nitration
   - Sulphonation
   - Chlorosulphonation
2. Combustion Reaction
3. Catalytic oxidation
4. Isomerisation
5. Aromatisation
6. pyrolysis

Combustion Reaction

Burning Hydrocarbon in the presence of oxygen to form CO_2 & H_2O → Combustion Reaction.

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow nCO_2 + (n+1) H_2O$$

alkane

$$C_nH_{2n} + \left(\frac{3n}{2}\right) O_2 \longrightarrow nCO_2 + nH_2O$$

alkene

$$C_nH_{2n-2} + \left(\frac{3n-1}{2}\right) O_2 \longrightarrow nCO_2 + (n-1) H_2O$$

alkyne

Que

$$C_2H_6 + \left(\frac{3\times2+1}{2}\right) O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$C_2H_4 + (3) O_2 \longrightarrow 2CO_2 + 2H_2O$$

$$C_2H_2 + \left(\frac{5}{2}\right) O_2 \longrightarrow 2CO_2 + H_2O$$

DU=0 $C_3H_8 + \left(\frac{3\times3+1}{2}\right)O_2 \longrightarrow 3CO_2 + 4H_2O$

n=3

alkane

$\boxed{5O_2}$

DU=1 $C_3H_6 + \left(\frac{3\times3}{2}\right)O_2 \longrightarrow 3CO_2 + 3H_2O$

alkene

$4.5\,O_2$

DU=2 $C_3H_4 + \left(\frac{3\times3-1}{2}\right)O_2 \longrightarrow 3CO_2 + 2H_2O$

alkyne

$4O_2$

PHOTO HALOGENATION

Chemical Reaction of Alkane

1. Halogenation
2. Nitration
3. Sulphonation
4. Combustion
5. Catalytic oxidation
6. Pyrolysis

Halogenation / Photohalogenation

Substitution of Hydrogen by Halogen in presence of very High Temp produces alkyl Halide is k/a Halogenation

$$R—H + X_2 \xrightarrow[\text{Sunlight, UV-rays, High Temp (300-500°C)}]{h\nu} R—X + H—X$$

R—H: alkane (less Reactive)

R—X: alkyl Halide

Eg
$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl \xrightarrow[h\nu]{Cl_2} CH_2Cl_2 + HCl \xrightarrow[h\nu]{Cl_2} CHCl_3 + HCl \xrightarrow[h\nu]{Cl_2} CCl_4$$

Mechanism

(i) Chain initiation step (ΔH = +ve endothermic)

$$:\ddot{Cl}—\ddot{Cl}: \xrightarrow{\Delta} 2Cl^{\bullet}$$

(ii) chain propagation step (ΔH = −ve exothermic)

(a) $Cl^{\bullet} + CH_4 \xrightarrow[\text{slow step}]{\text{RDS}} CH_3^{\bullet} + HCl$ (RDS → Rate determining step)

(b) $CH_3^{\bullet} + Cl_2 \longrightarrow CH_3—Cl + Cl^{\bullet}$ (Regenerate) ↓ infinite Reaction

(iii) Chain Termination step (ΔH = −ve exothermic)

$$Cl^{\circ} + Cl^{\circ} \longrightarrow Cl_2$$

$$CH_3^{\circ} + CH_3^{\circ} \longrightarrow CH_3—CH_3$$

$$CH_3^{\circ} + Cl^{\circ} \longrightarrow CH_3—Cl$$

Chain intiation step $\xrightarrow{\text{identify}}$ Radical is present on product side.

Chain propagation step $\xrightarrow{\text{"}}$ Radical is present on Reactant as well as product Side.

Chain Termination step $\xrightarrow{\text{"}}$ Radical is present on Reactant Side.

Imp points

① intermediate → Free Radical

② This is a Free Radical substitution Reaction. (FRSR)

③ Reactivity : $F_2 > Cl_2 > Br_2 > I_2$

F_2 ↓ Highly exothermic ↓ explosive

I_2 ↓ Highly Endothermic

④ Reactivity : $CH_4 > CD_4 > CT_4$ (kinetic isotopic effect)

C—H, C—D, C—T

⑤ Reactivity ↓ Stab of Free Radical



$> CH_2{=}CH{-}\dot{C}H_2 > Me_3\dot{C} > Me_2\dot{C}H > Me{-}\dot{C}H_2 > \dot{C}H_3$

(6) CH_4 (excess) $+ Cl_2 \longrightarrow CH_3Cl$ Chloromethane

$CH_4 + Cl_2$ (excess) $\longrightarrow CCl_4$ Carbon Tetrachloride (used as Fire extinguisher)

or

per Chloro Methane

or

Trade name → Pyrene

(7) $CH_4 + Cl_2$

- $\xrightarrow{h\nu / \text{UV-rays} / \text{sunlight} / 300\text{-}500^\circ C}$ $CH_3Cl + HCl$
- $\xrightarrow[\text{Room temp}]{\text{Dark}}$ ✗✗
- $\xrightarrow[300^\circ C]{\text{Dark}}$ $CH_3-Cl + HCl$
- $\xrightarrow[12{:}00 \text{ noon}]{\text{Bright Sunlight}}$ C_{black} (coke) $+ HCl$

Bright Sunlight → High intensity of Sunlight

Fluorination (Highly exothermic)

$$CH_4 + F_2 \xrightarrow{\text{explosive}} C_{black} + HF$$
(coke)

<u>note</u> → To prevent damage from High exothermic reaction → liq N_2 is added as a coolant. (→ −196°C)
→ N_2 creates inert atmosphere.
↓
non reactive atmosphere.

Bromination

Bromination is same as chlorination.
Bromination is less vigourous reaction than Fluorination.

Iodination (Highly endothermic)

$$CH_4 + I_2 \uparrow \rightleftharpoons CH_3I + HI$$

HI → very strong Reducing agent (It reduces CH_3I to CH_4)

* we add oxidising agent like (HNO_3 | HIO_3) to take this reaction forward.

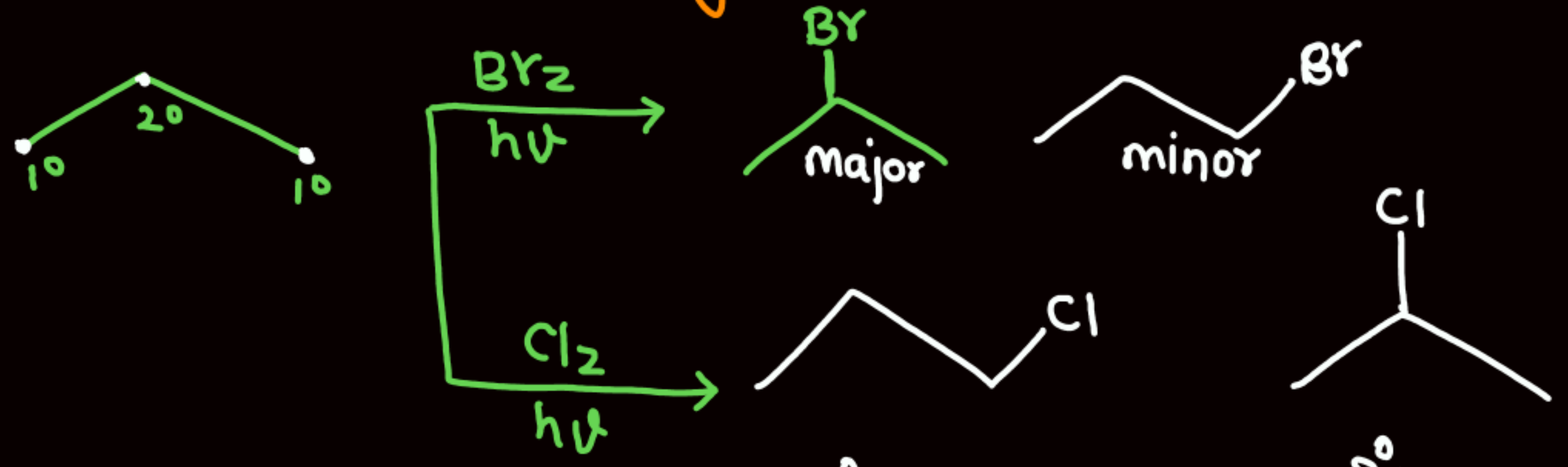
$$\underset{OA}{HIO_3} + \underset{RA}{H\overset{-1}{I}} \rightarrow \overset{0}{I_2} + H_2O$$

→ HI consume
I_2 concentration ↑

Reactivity v/s Selectivity

Per 'H' Reactivity Ratio	1°H	2°H	3°H
Cl_2 →	1	3.8	5.0
Br_2 →	1	82	1600

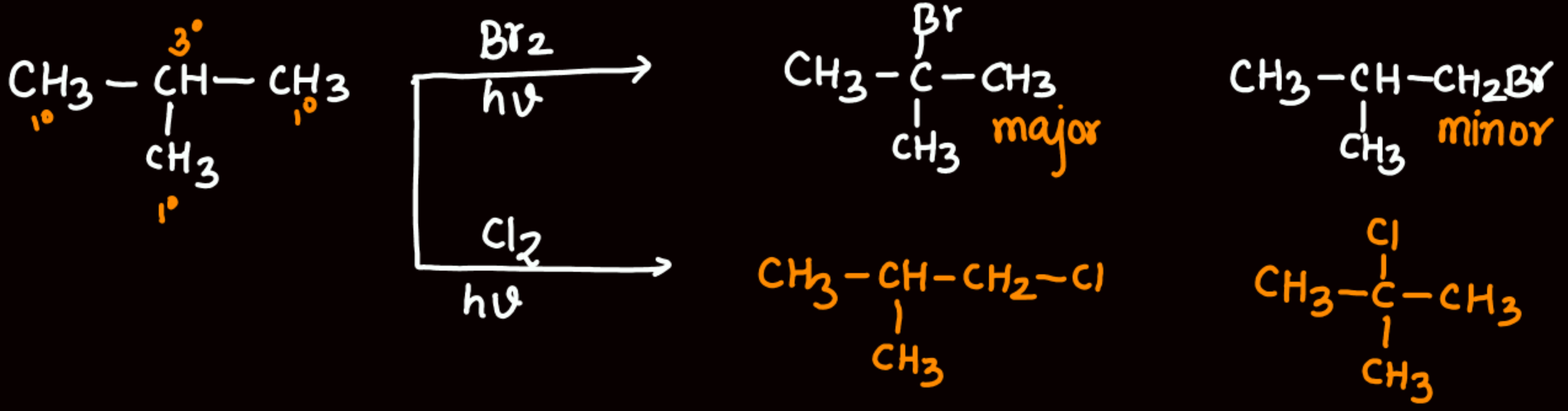
* Bromination process → High Selective Low Reactive → 3°H > 2°H > 1°H
* Chlorination process → High Reactive low Selective → दिमाग लगाना पड़ेगा ।



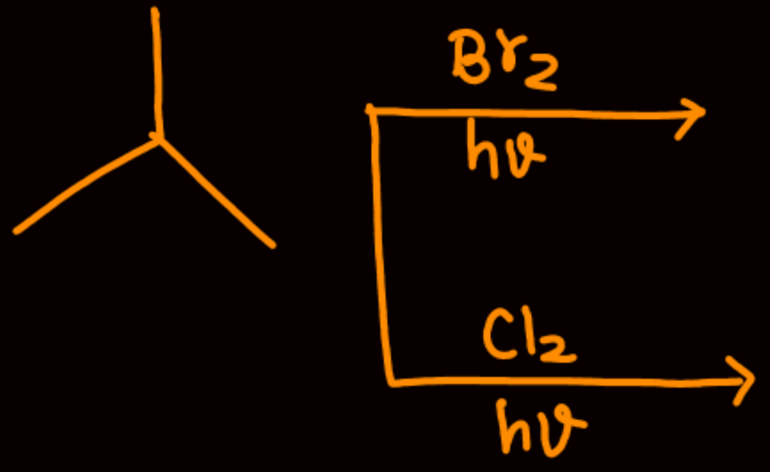
1°H × RR
6 × 1
6

2°H × RR
2 × 3.8
7.6

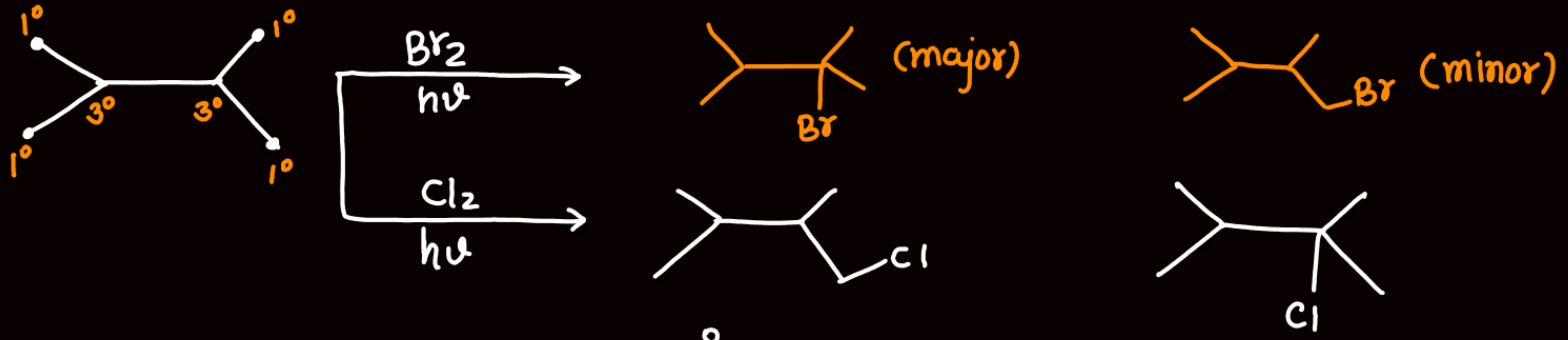
Major



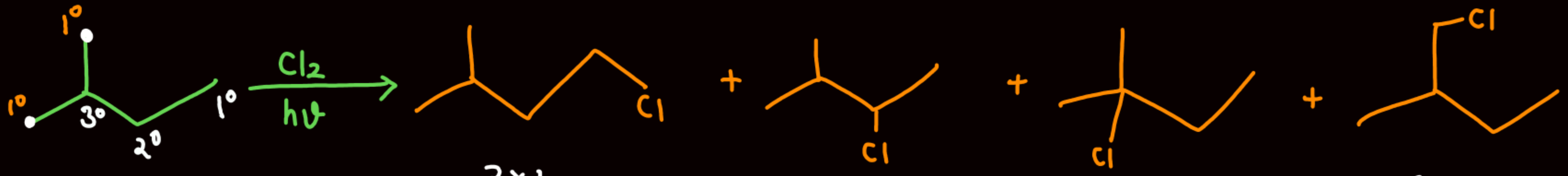
$1^\circ H \times RR$	$3^\circ H \times RR$
9×1	1×5
9	5
(major)	(minor)



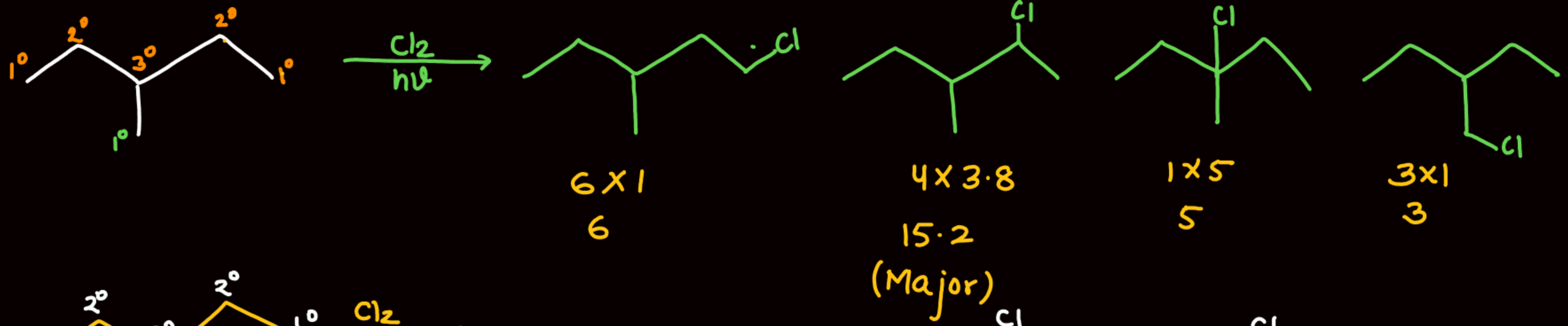
Same



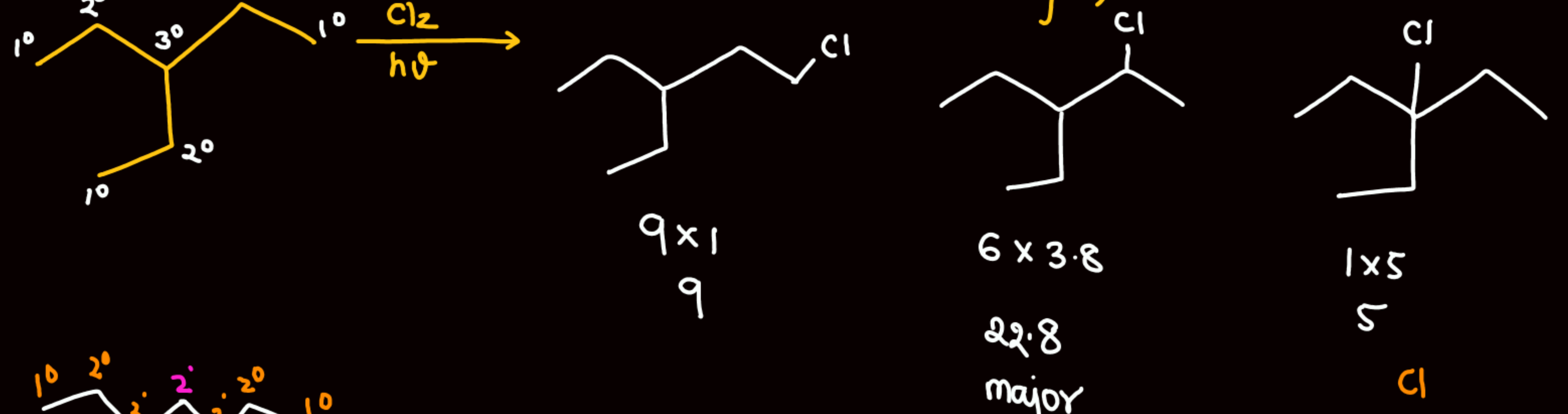
1°H × RR	3°H × RR
12 × 1	2 × 5
(12)	(10)
Major	Minor



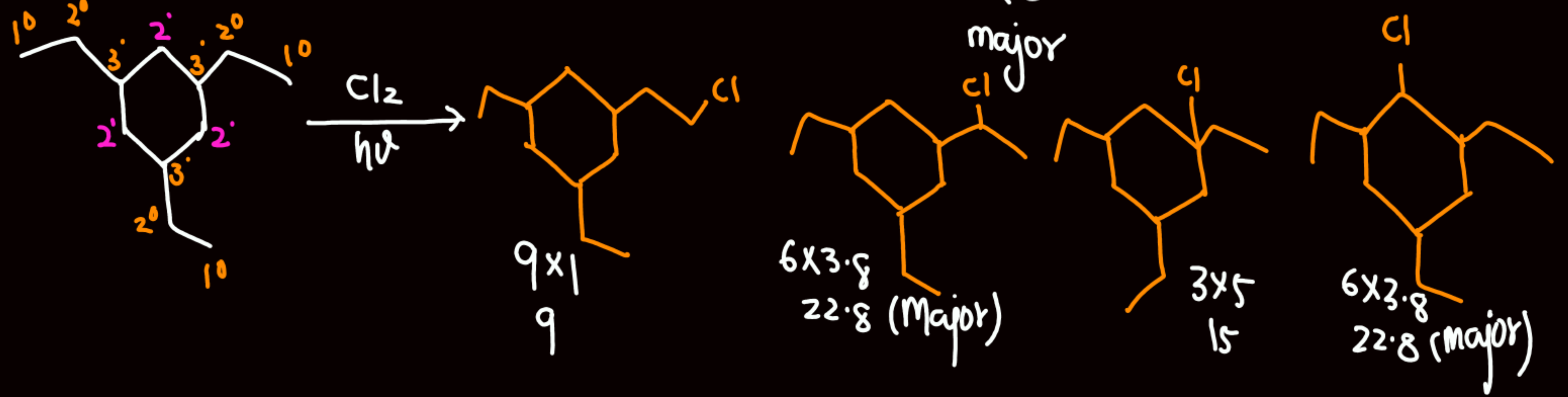
3×1	2×3·8	1×5	6×1
3	7·6	5	6
	Major		



1°
2°
3°
2°
1°
1°
Cl2
hν
Cl
6×1
6
Cl
4×3.8
15.2
(Major)
Cl
1×5
5
Cl
3×1
3



1°
2°
3°
2°
1°
2°
1°
Cl2
hν
Cl
9×1
9
Cl
6×3.8
22.8
major
Cl
1×5
5

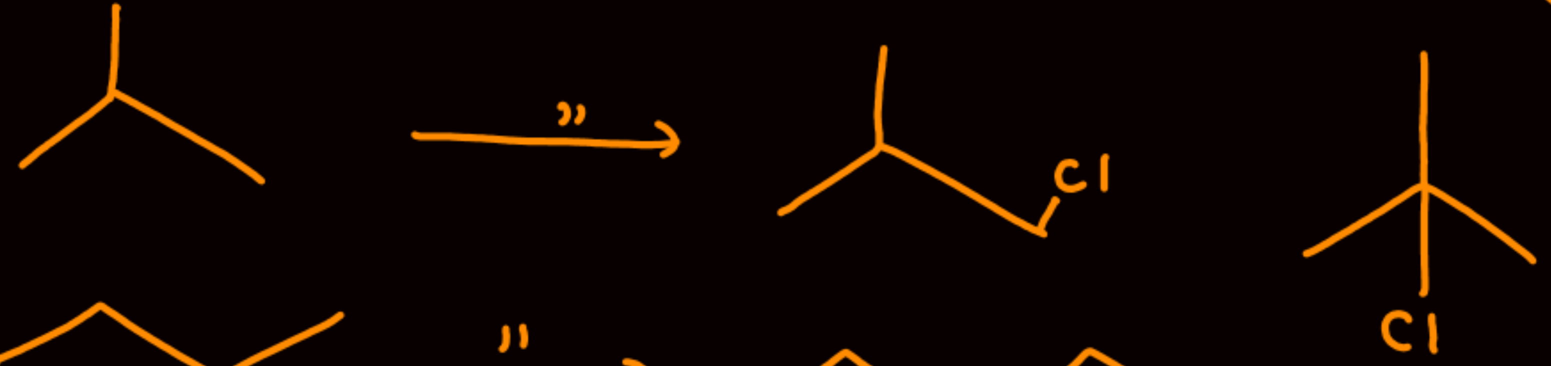


1°
2°
3°
2°
3°
2°
1°
2°
2°
3°
2°
1°
Cl2
hν
Cl
9×1
9
Cl
6×3.8
22.8 (Major)
Cl
3×5
15
Cl
6×3.8
22.8 (major)

Type-2 Ques | write monochlorinated prod

Q 

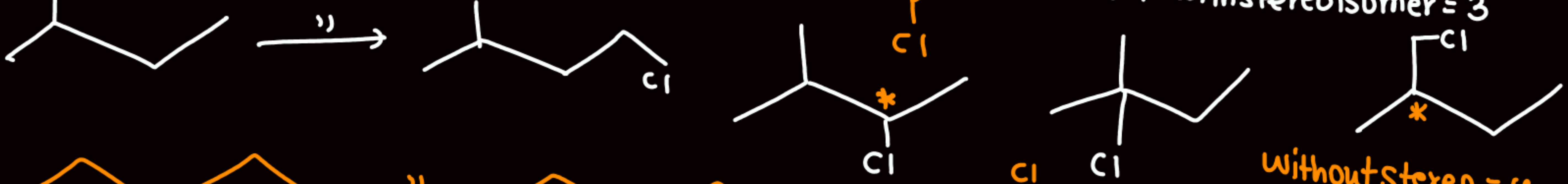
(2)

Q 

(2)

Q 

MCP without stereoisomers = 2
MCP with stereoisomer = 3

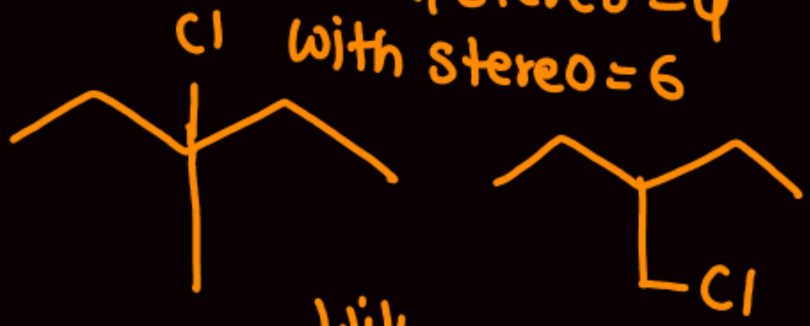
Q 

without stereo = 4
with stereo = 6

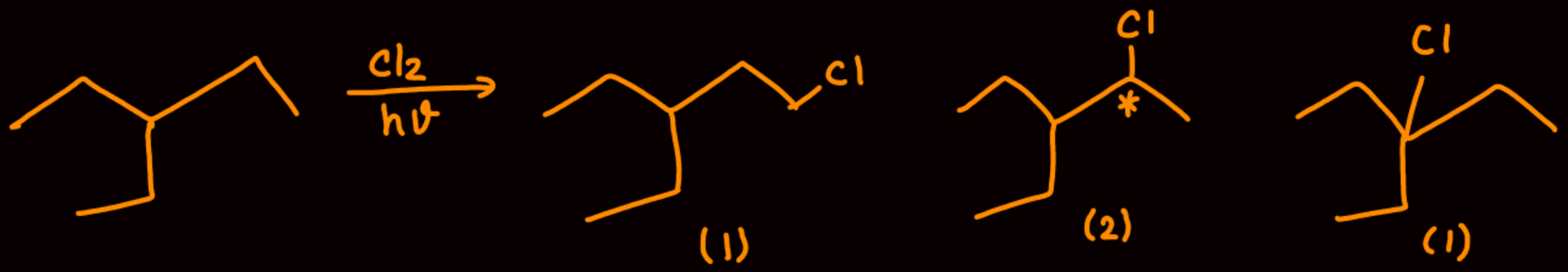
Q 

(2)

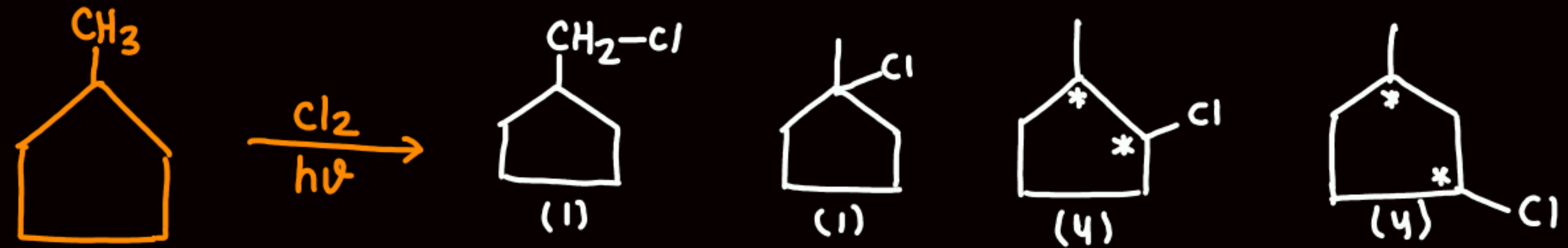
(4)



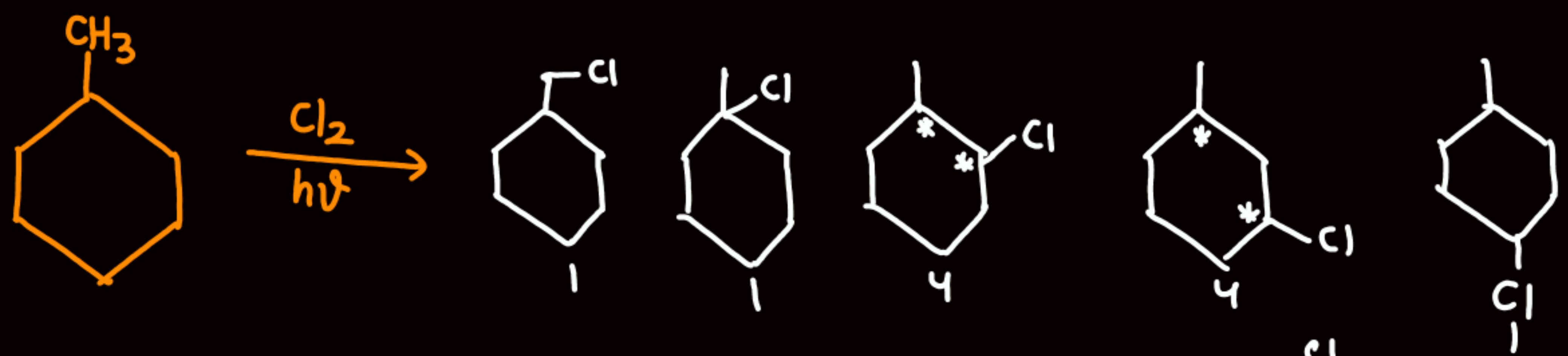
with stereo = 8
without stereo = 4



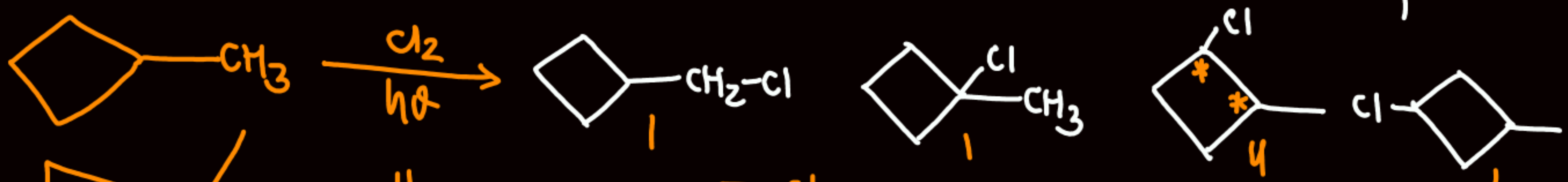
without stereo = 3
with stereo = 4



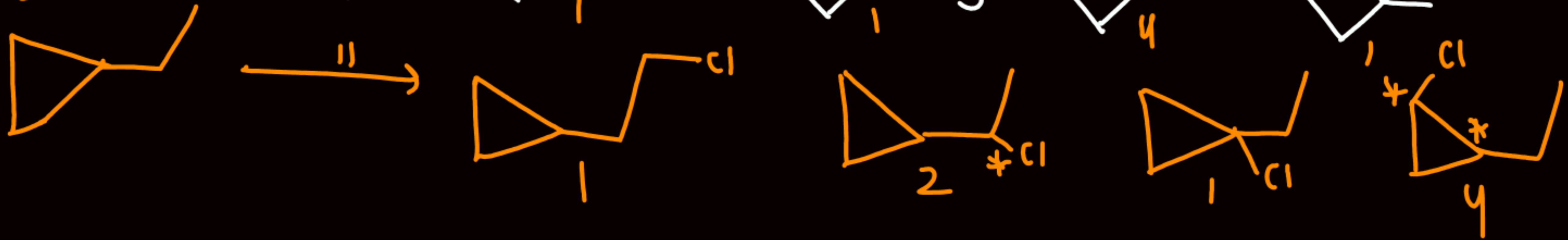
without stereo = 4
without stereo = 10



without stereo = 5
with stereo = 11



without stereo = 4
with stereo = 7



Without stereo = 4
With stereo = 8

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[h\nu]{Br_2}$$ How many major products are possible

$$CH_3-\overset{*}{C}H(Br)-CH_2-CH_3 \quad (2)$$

Nitration

$$CH_3-CH_3 + HNO_3 \xrightarrow{400°c-500°c} CH_3-CH_2-NO_2 + H_2O$$

$$CH_3-CH_3 + HO-NO_2 \xrightarrow{,,} CH_3-CH_2-NO_2 + H_2O$$

$H\dot{O}$ $\;\dot{N}O_2$

$$CH_3-NO_2 + CH_3-OH$$

- Very High Temp (400-500°c)
- Reagent – HNO_3 (nitric acid)
- all possible bonds are broken and nitroalkane is formed → C–H bond break / → C–C bond break
- Free Radical Mechanism

Eg $CH_3-CH_2-CH_3 + HNO_3 \longrightarrow$

$CH_3-CH_2-CH_2-NO_2 + H_2O$

$CH_3-CH(NO_2)-CH_3 + H_2O$

$CH_3-CH_3-NO_2 + CH_3-OH$

$CH_3-NO_2 + CH_3-CH_2-OH$

Sulphonation

1. 1°H is replaced by SO_3H
2. Temp → 400°C
3. Reagent → Oleum $H_2S_2O_7$

   Fuming H_2SO_4 : $H_2SO_4 + SO_3$ gas Fumes

   Mixture of (Conc H_2SO_4 & SO_3)

* Free Radical Mechanism

> **note** → Smaller alkanes form sulphonic acid by reaction with SO_3.
>
> $CH_4 + SO_3 \rightarrow CH_3-SO_3H$
>
> $CH_3-CH_3 + SO_3 \rightarrow CH_3-CH_2-SO_3H$
>
> $CH_3-CH_2-CH_2-CH_3 + SO_3 \longrightarrow CH_3-CH_2-CH_2-CH_2-SO_3H$

4. 6 Carbon or Higher alkane gives sulphonation rxn (1°H) / Tertiary alkane gives sulphonation. (alkane → 3°H)

Q. $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ + Fuming H_2SO_4 or $H_2S_2O_7$ or ($H_2SO_4 + SO_4$) → $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-SO_3H$

Q. 

Tertiary Alkane

Chloro-Sulphonation
(Reed Reaction)

* Reagent → $SO_2 + Cl_2$ & $h\nu$
* 1°H will be replaced by SO_2Cl.

$$CH_3-CH_2-CH_3 \xrightarrow[h\nu]{(SO_2+Cl_2)} CH_3-CH_2-CH_2-SO_2Cl \xrightarrow{H_2O} CH_3-CH_2-CH_2-SO_3H$$

Catalytic oxidation

alkane →

- Red Hot Fe/Cu tube, 100 atm, 523K → alcohol
- Mo_2O_3 → aldehyde
- $Mn(CH_3COO)_2$ → carboxylic acid

$$CH_4 + O_2 \xrightarrow[\text{Red Hot Cu tube}]{\text{Red Hot Fe tube or}} CH_3OH$$

$$CH_3-CH_3 + O_2 \xrightarrow{''} CH_3-CH_2-OH$$

$$CH_3-CH_2-CH_3 + O_2 \xrightarrow{''} CH_3-CH_2-CH_2-OH$$

$$CH_4 + Mo_2O_3 \longrightarrow H-\overset{O}{\overset{||}{C}}-H$$

$$CH_3-CH_3 + '' \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-H$$

$$CH_3-CH_2-CH_2 + '' \longrightarrow CH_3-CH_2-\overset{O}{\overset{||}{C}}-OH$$

$$CH_4 + Mn(CH_3COO)_2 \longrightarrow H-\overset{O}{\overset{||}{C}}-OH$$

$$CH_3-CH_3 + '' \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-OH$$

$$CH_3-CH_2-CH_3 + '' \longrightarrow CH_3-CH_2-\overset{O}{\overset{||}{C}}-OH$$

Isomerisation

$CH_3-CH_2-CH_2-CH_3$ $\xrightarrow[\text{Conc HCl}]{\text{Anhydrous AlCl}_3}$ $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$

alkane (Butane) → (Iso butane)

Straight chain alkane → Branched chain Alkane

Low Quality Fuel → High Quality Fuel

Q



Q

$CH_3-(CH_2)_4-CH_3$ $\xrightarrow[\text{Conc HCl}]{\text{anhy AlCl}_3}$ $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3$ or $CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

Q

$CH_3-(CH_2)_6-CH_3$ $\xrightarrow{\text{"}}$ Iso-Octane

n-octane

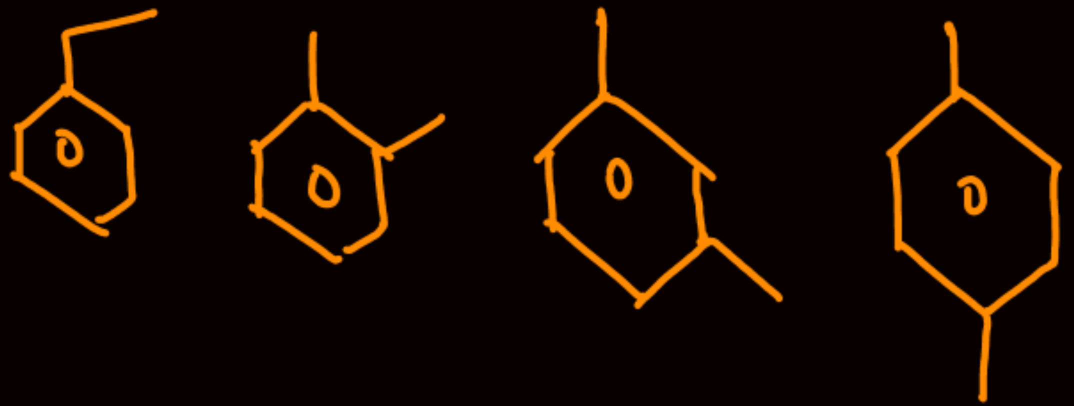
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$

Aromatization

6 Carbon or Higher Alkane $\xrightarrow[773K]{Cr_2O_3 \text{ or } V_2O_5 \text{ or } Mo_2O_3}$ Aromatic Comp (Benzene / its derivative)

$CH_3-(CH_2)_4-CH_3 \xrightarrow[773K]{Cr_2O_3/V_2O_5/Mo_2O_3}$ 

$CH_3-(CH_2)_5-CH_3 \xrightarrow[773K]{''}$ 

$CH_3-(CH_2)_6-CH_3 \xrightarrow[773K]{''}$ 

Cracking / Pyrolysis

- At 773K alkanes break down to form lower alkanes/alkenes/H_2 gas.
- Free Radical mechanism.

$$CH_4 \xrightarrow[(500^\circ C)]{773K} C + 2H_2$$

C black (Coke)

$$CH_3-CH_3 \xrightarrow{''} CH_2=CH_2 + H_2$$

$2CH_4$

$$CH_3-CH_2-CH_3 \xrightarrow{''} CH_3-CH=CH_2 + H_2$$

$$CH_4 + CH_2=CH_2$$

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{''} CH_3-CH_2-CH=CH_2 + H_2$$

$$CH_3-CH=CH-CH_3 + H_2$$

$$CH_3-CH=CH_2 + CH_4$$

$$CH_3-CH_3 + CH_2=CH_2$$

Kerosene
↓
dodecane
↓
Alkane of 12 Carbon

Alkene

Method of Preparation

Hydrocarbon (Alkene)

Method of Preparation

1. Alkyne ⟶ Alkene
   $-C\equiv C-$ ⟶ $>C=C<$
   → Controlled Hydrogenation.
   → Hydrogenation with poison Catalyst.
2. Alkyl Halide ⟶ Alkene
3. Alcohol ⟶ Alkene
4. Aldehyde/ketone ⟶ Alkene
5. Carboxylic acid ⟶ Alkene
6. Ester ⟶ Alkene

Alkyne → Alkene

- **Use of Poison Catalyst**

↓

Poison added to Catalyst occupies metal surface

↓

H_2 gas is less adsorb

↓

less Reaction

↓

Controlled Hydrogenation

$\xrightarrow[Pd-C]{H_2}$ → Palladised Carbon

$\xrightarrow[Pd-CaCO_3]{H_2}$ → Lindlar's Catalyst

$\xrightarrow[Pd-BaSO_4]{H_2}$ → Rosenmund catalyst

$\xrightarrow[Ni_2B]{H_2}$ (nickel Boride) → P_2 Catalyst

} Syn addition of H_2

↓

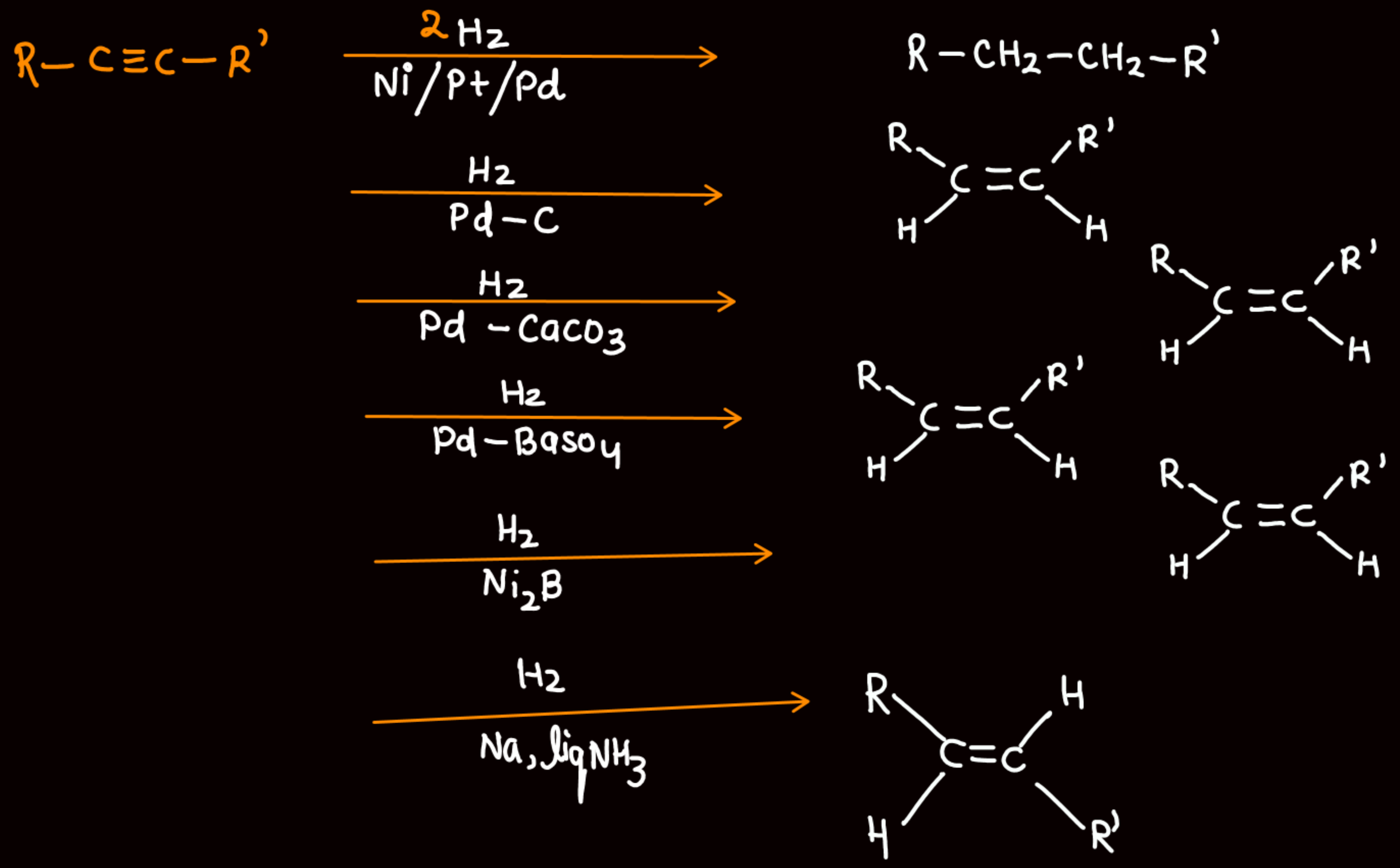
Cys alkene

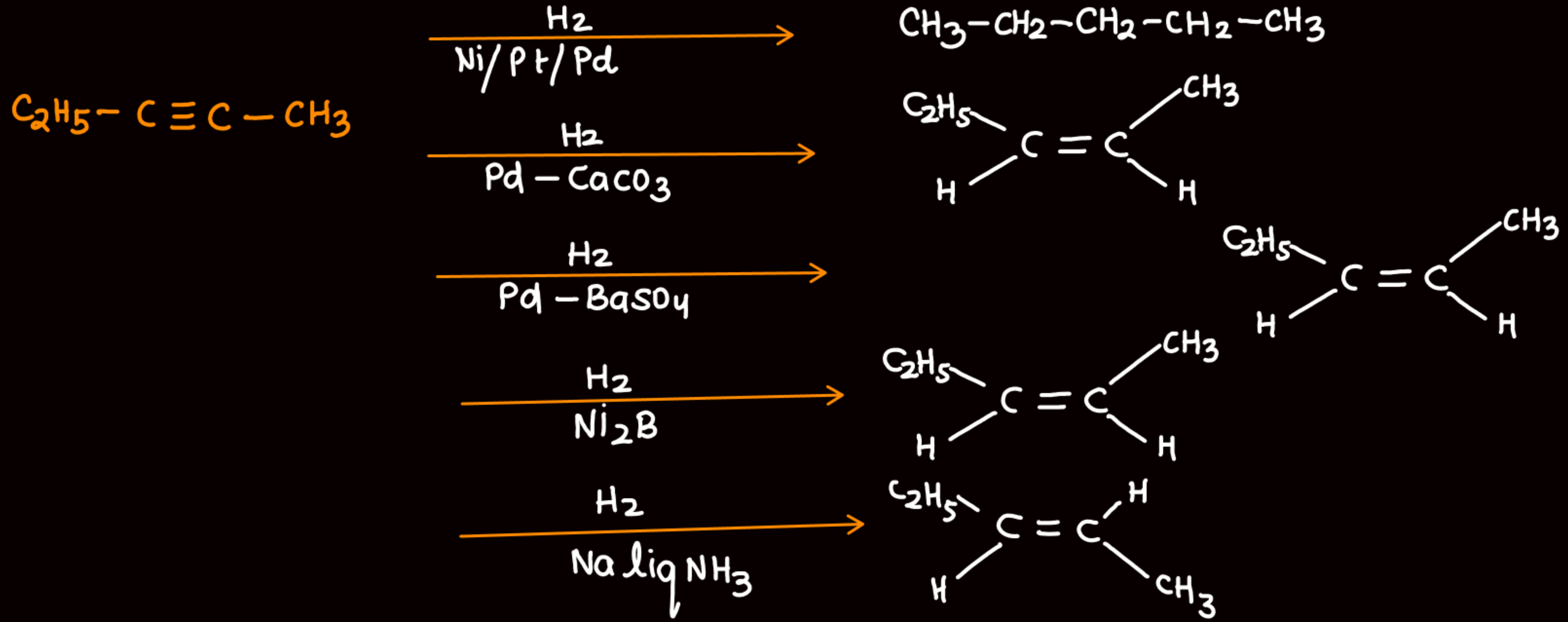
$\xrightarrow[Na, liq NH_3]{H_2}$ → Birch Reduction

} Anti addition of H_2

↓

Trans Alkene


R—C≡C—R'
2H2
Ni/Pt/Pd
R—CH2—CH2—R'
H2
Pd—C
H2
Pd —CaCO3
H2
Pd—BaSO4
H2
Ni2B
H2
Na, liq NH3
R
R'
H
H


C2H5 – C ≡ C – CH3
H2
Ni/Pt/Pd
CH3–CH2–CH2–CH2–CH3
H2
Pd – CaCO3
C2H5
CH3
C = C
H
H
H2
Pd – BaSO4
C2H5
CH3
C = C
H
H
H2
Ni2B
C2H5
CH3
C = C
H
H
H2
Na liq NH3
C2H5
H
C = C
H
CH3

$CH_3-C\equiv CH$

Terminal Alkyne

$$CH_3-C\equiv CH \xrightarrow[Ni/Pt/Pd]{H_2} CH_3-CH_2-CH_3$$

$$\xrightarrow[Pd-C]{H_2} CH_3(H)C=CH_2$$

$$\xrightarrow[Pd-CaCO_3]{H_2} CH_3(H)C=CH_2$$

$$\xrightarrow[Pd-BaSO_4]{H_2} CH_3(H)C=CH_2$$

$$\xrightarrow[Ni_2B]{H_2} CH_3(H)C=CH_2$$

$$\xrightarrow[Na-liq\ NH_3]{H_2} CH_3-C\equiv C^{\ominus}\ Na^{+} + NH_4^{+}$$

NH_3 ↓ Base

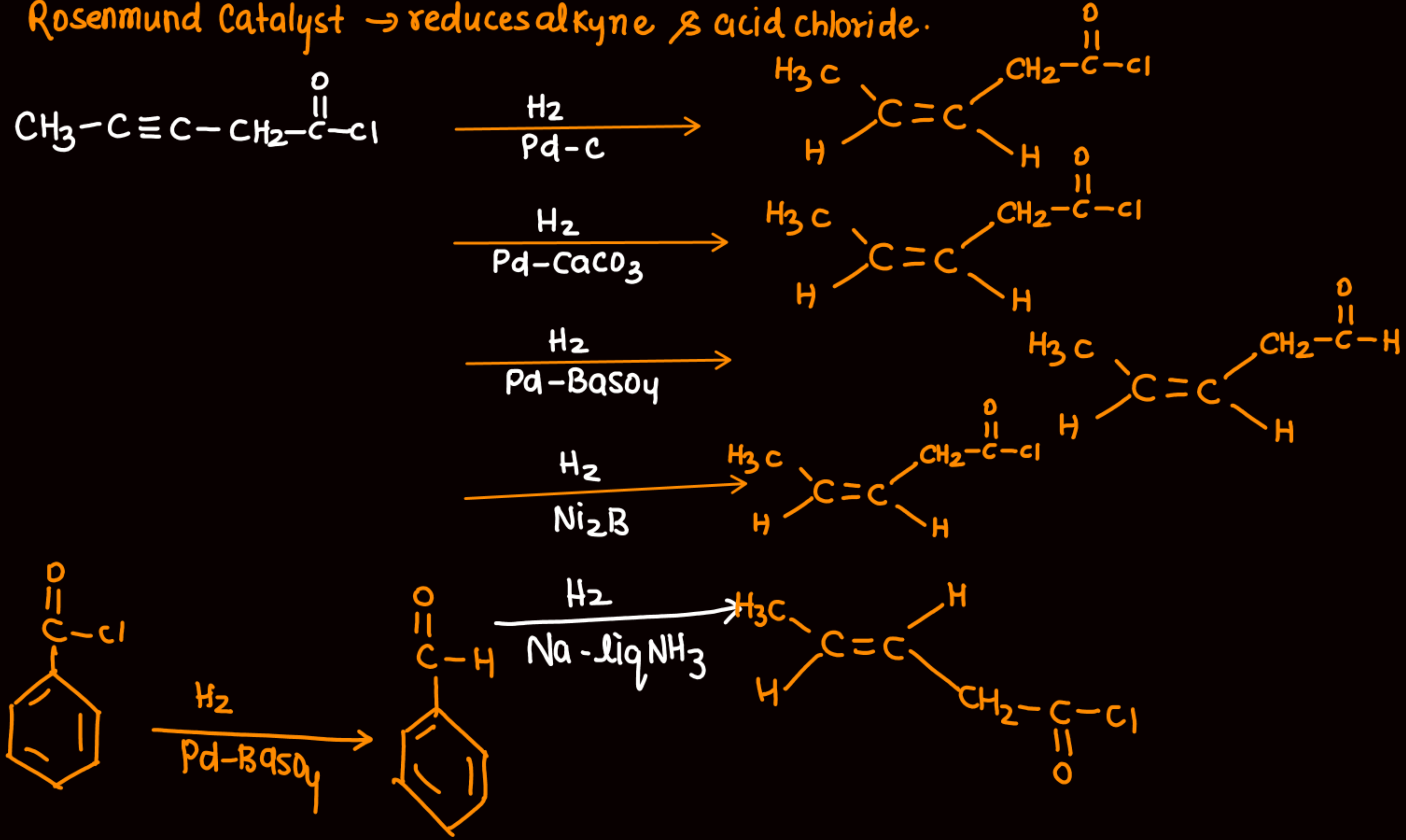
note → Birch Reduction gives acid-base reaction with terminal alkyne

Birch Reduction ↓ Base

terminal alkyne ↓ acidic H

note Rosenmund Catalyst → reduces alkyne & acid chloride.

Q



$R-CH=CH_2$

or

$R-CH=CH-R'$

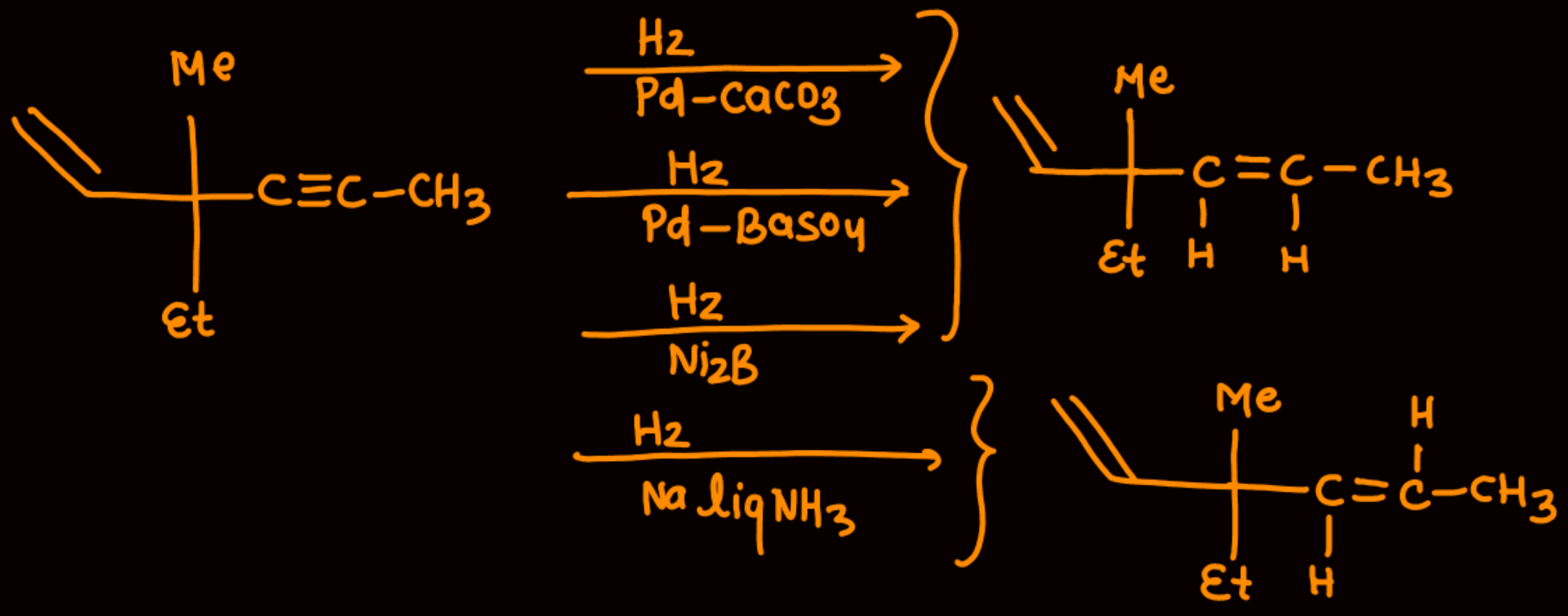
$\xrightarrow[Pd-C]{H_2}$ ×

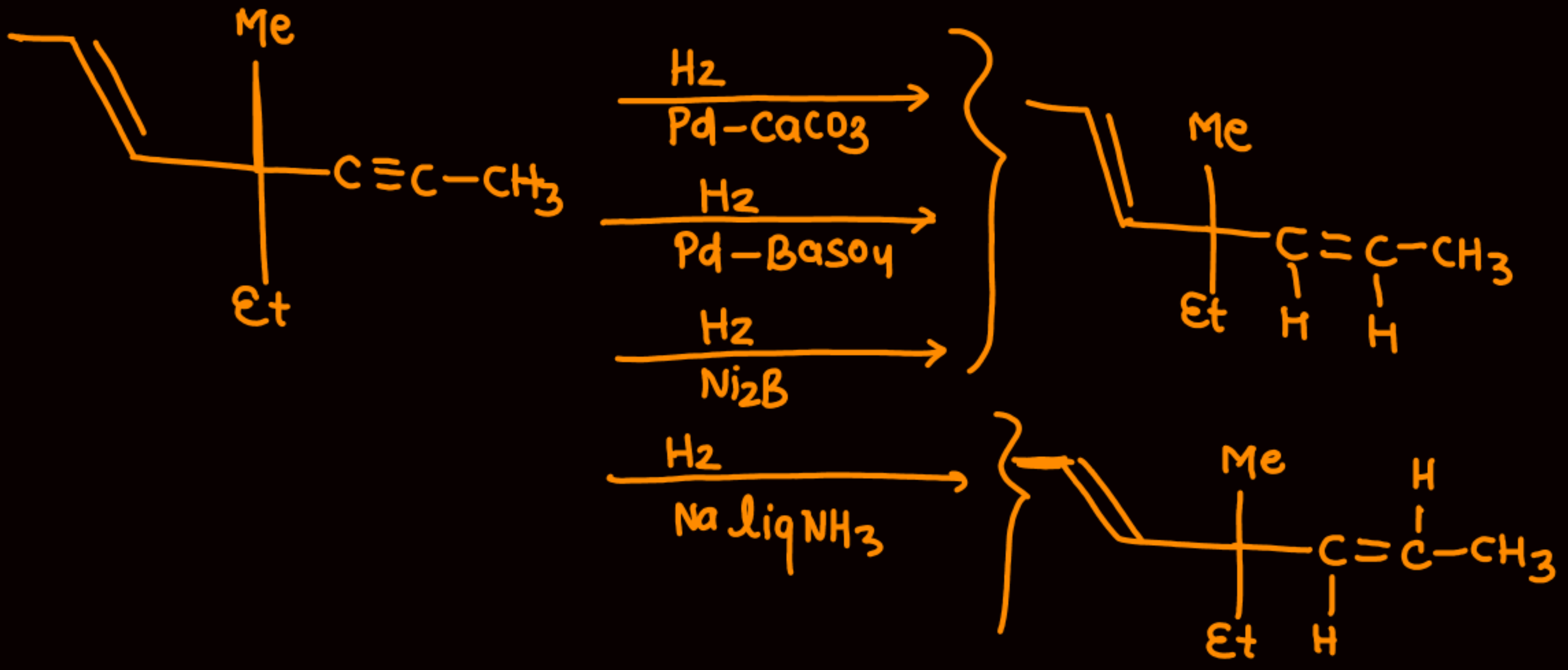
$\xrightarrow[Pd-CaCO_3]{H_2}$ ×

$\xrightarrow[Pd-BaSO_4]{H_2}$ ×

$\xrightarrow[Ni_2B]{H_2}$ ×

$\xrightarrow[Na-liq\ NH_3]{H_2}$ ×





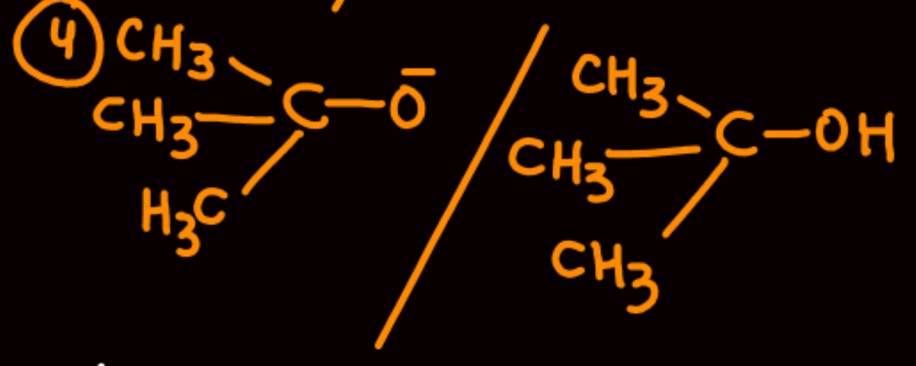
ALKYL HALIDE TO ALKENE

MonoHalide

$R-CH_2-CH_2-X \xrightarrow{\text{① alc KOH / } \Delta \text{ or } NaNH_2/NH_3} R-CH=CH_2 + HX$

② $R-O^- / R-OH$

③ CH_3-O^- / CH_3-OH

④ 

Strong Base (①–④)

- DeHydroHalogenation → Removal of HX
- alcoholic KOH → KOH + R–ÖH
- ROH + RÖH → RO^- / ROH (KO^- (strong base))

DiHalide

$R-CH(X)-CH_2(X) \xrightarrow{\text{① Zn-dust}/\Delta} R-CH=CH_2$

② NaI/acetone

③ Ag-Powder

④ Na-ether

- DeHalogenation → Removal of X_2

Que

$$CH_3-CH_2-CH_2-Cl \xrightarrow{alc\,KOH/\Delta} CH_3-CH=CH_2 + HCl$$

$$CH_3-CH_2-C(Cl)(CH_3)-CH_3 \xrightarrow{alc\,KOH/\Delta} CH_3-CH=C(CH_3)-CH_3 + HCl \quad\quad CH_3-CH_2-C(CH_3)=CH_2 + HCl$$

9 αH (stable) (Major) — 5 αH

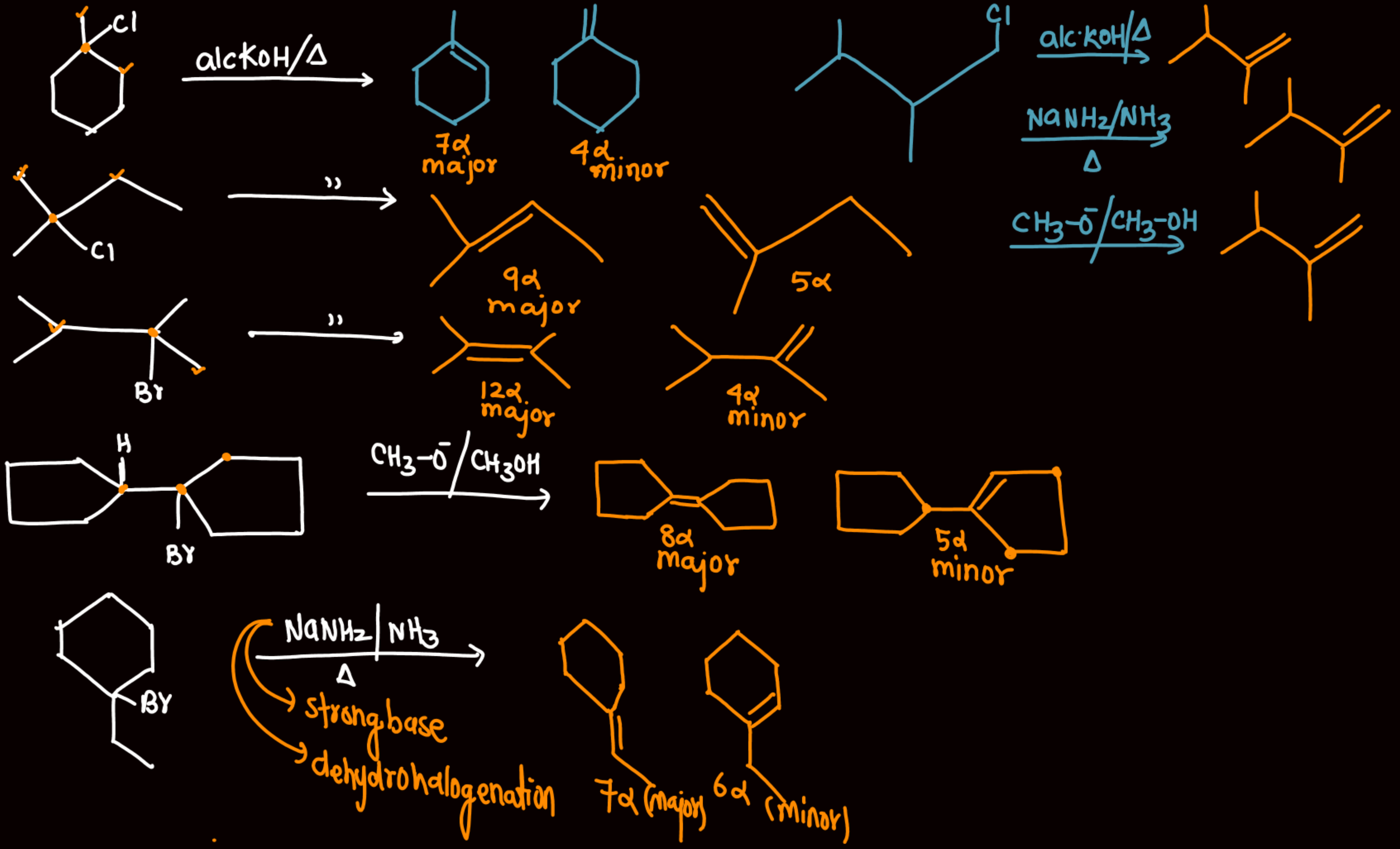
note → alcKOH/Δ is a strong base
dehydrohalogenation

$$CH_3-C(CH_3)_2-C(Cl)(H)-CH_2 \xrightarrow{alc\,KOH/\Delta} CH_3-C(CH_3)_2-C(H)=CH_2$$

$$CH_3-CD_2-CH(Cl)-CH_3 \xrightarrow{alc\,KOH/\Delta} CH_3-CD=CH-CH_3 + DCl \quad + \quad CH_3-CD_2-CH=CH_2 + HCl \text{ (major)}$$

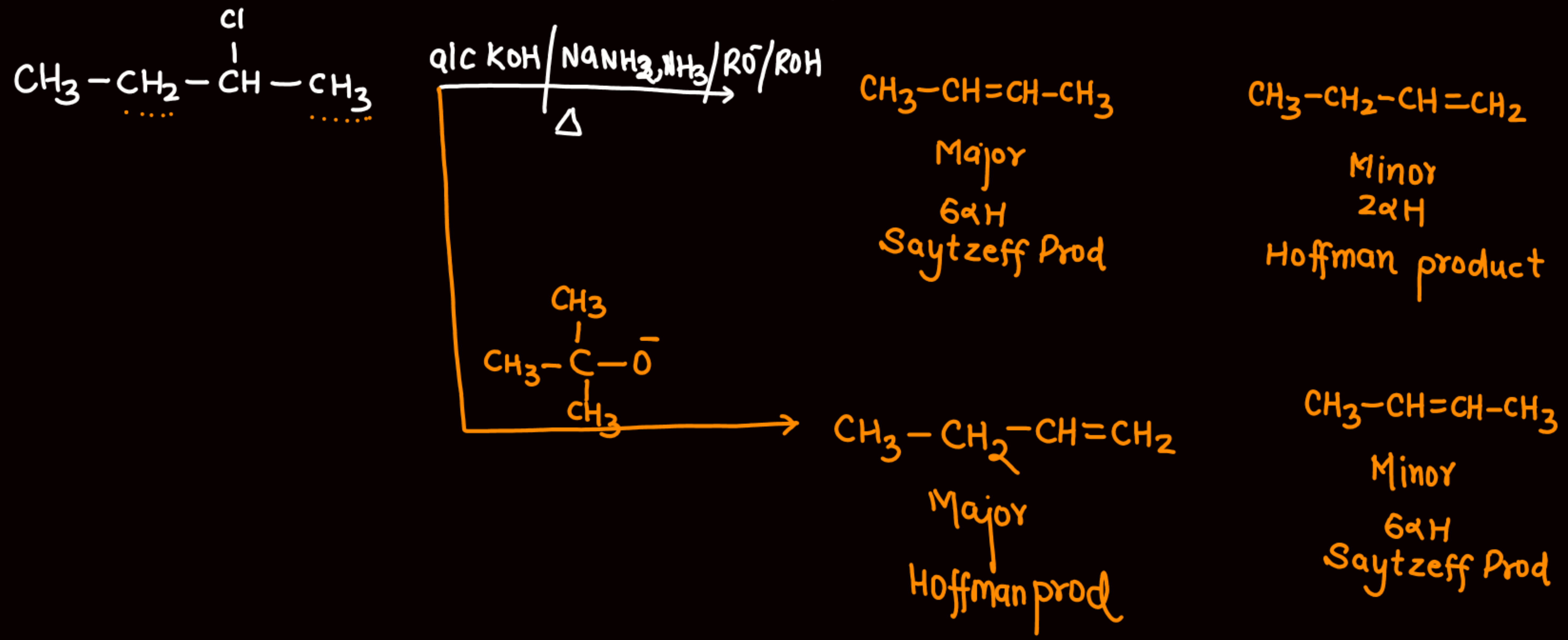
Bond strength → C–H < C–D < C–T

C–H ↓ easily break

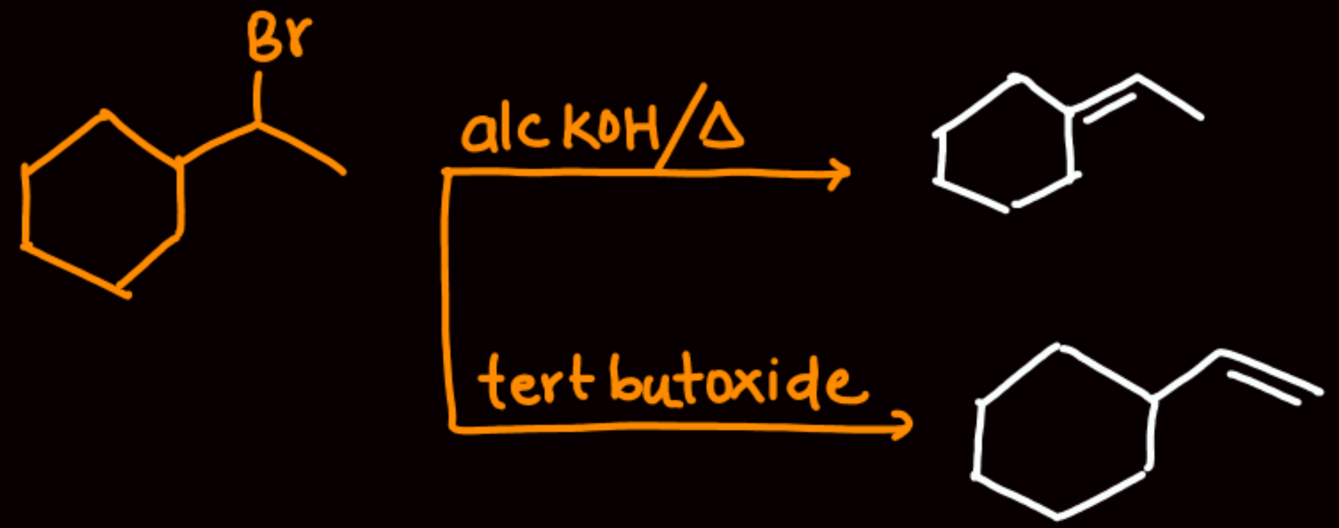

Cl
alcKOH/Δ
7α major
4α minor
Cl
alc·KOH/Δ
NaNH2/NH3
Δ
CH3-O⁻/CH3-OH
"
Cl
9α major
5α
"
Br
12α major
4α minor
H
CH3-O⁻/CH3OH
BR
8α major
5α minor
NaNH2/NH3
Δ
BR
strong base
dehydrohalogenation
7α (major)
6α (minor)

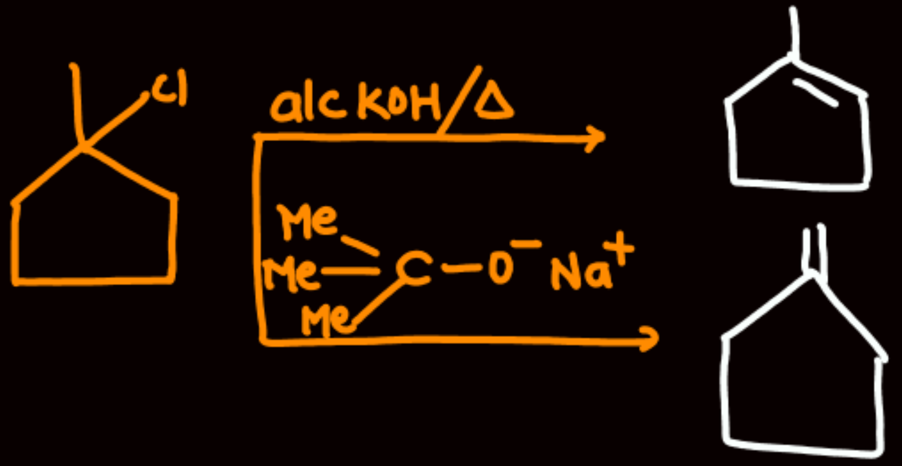
note → Bulky Base (→ tert-butoxide) gives Hoffman Product as major product.

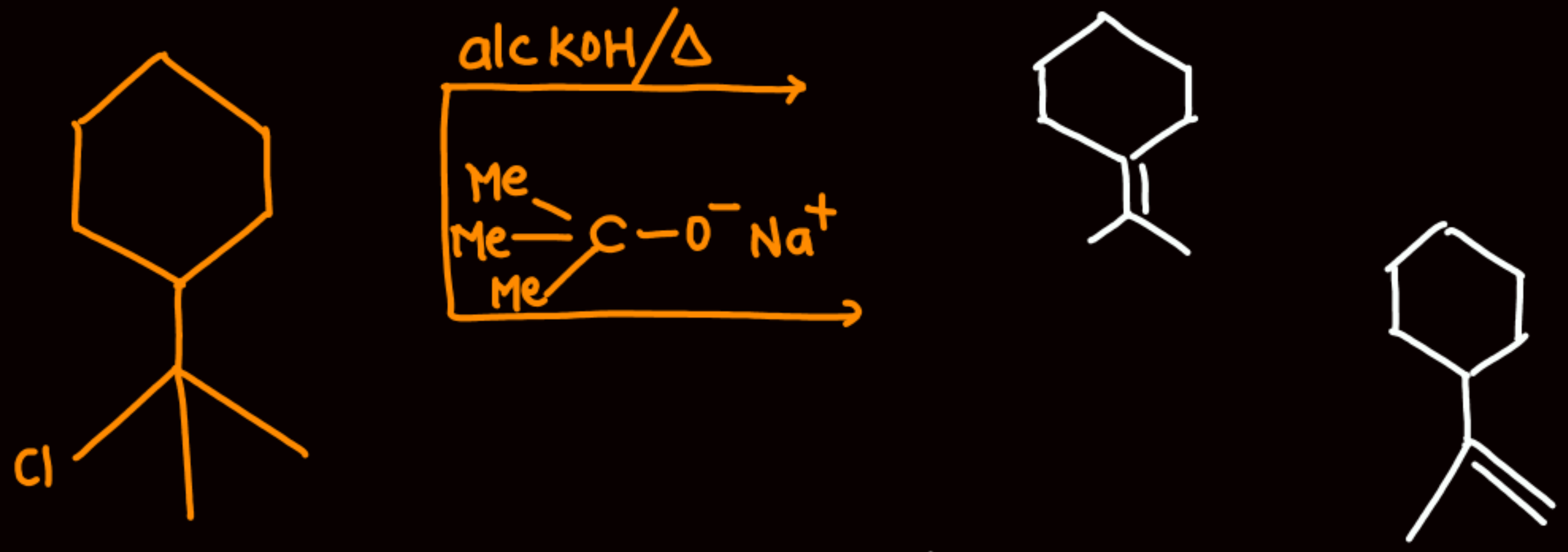
→ ———— attacks on less hindered Hydrogen.

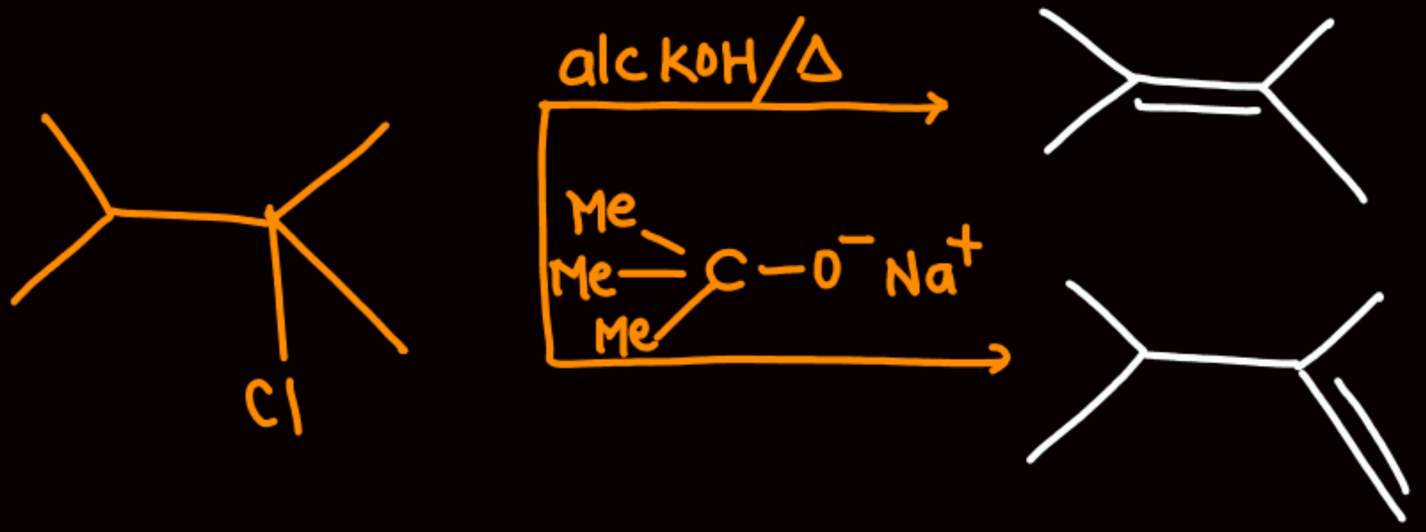


Q Write major Prod.









Hydrocarbon (Alkene)

Method of Preparation

1. Alkyne ⟶ Alkene
   $-C\equiv C-$ ⟶ $>C=C<$
   → Controlled Hydrogenation.
   → Hydrogenation with poison Catalyst.
2. Alkyl Halide ⟶ Alkene → dehydrohalogenation: alc KOH, alc NaOH, RO^-/ROH, $(CH_3)_3C-O^-/(CH_3)_3C-OH$
3. Alcohol ⟶ Alkene (Today's goal)
4. Aldehyde/ketone ⟶ Alkene
5. Carboxylic acid ⟶ Alkene
6. Ester ⟶ Alkene

Alkyne ⟶ Alkene

- **Use of Poison Catalyst**

  ↓

  Poison added to Catalyst occupies metal surface

  ↓

  H_2 gas is less adsorb

  ↓

  less Reaction

  ↓

  Controlled Hydrogenation

$\xrightarrow[Pd-C]{H_2}$ ⟶ Palladised Carbon

$\xrightarrow[Pd-CaCO_3]{H_2}$ ⟶ Lindlar's Catalyst

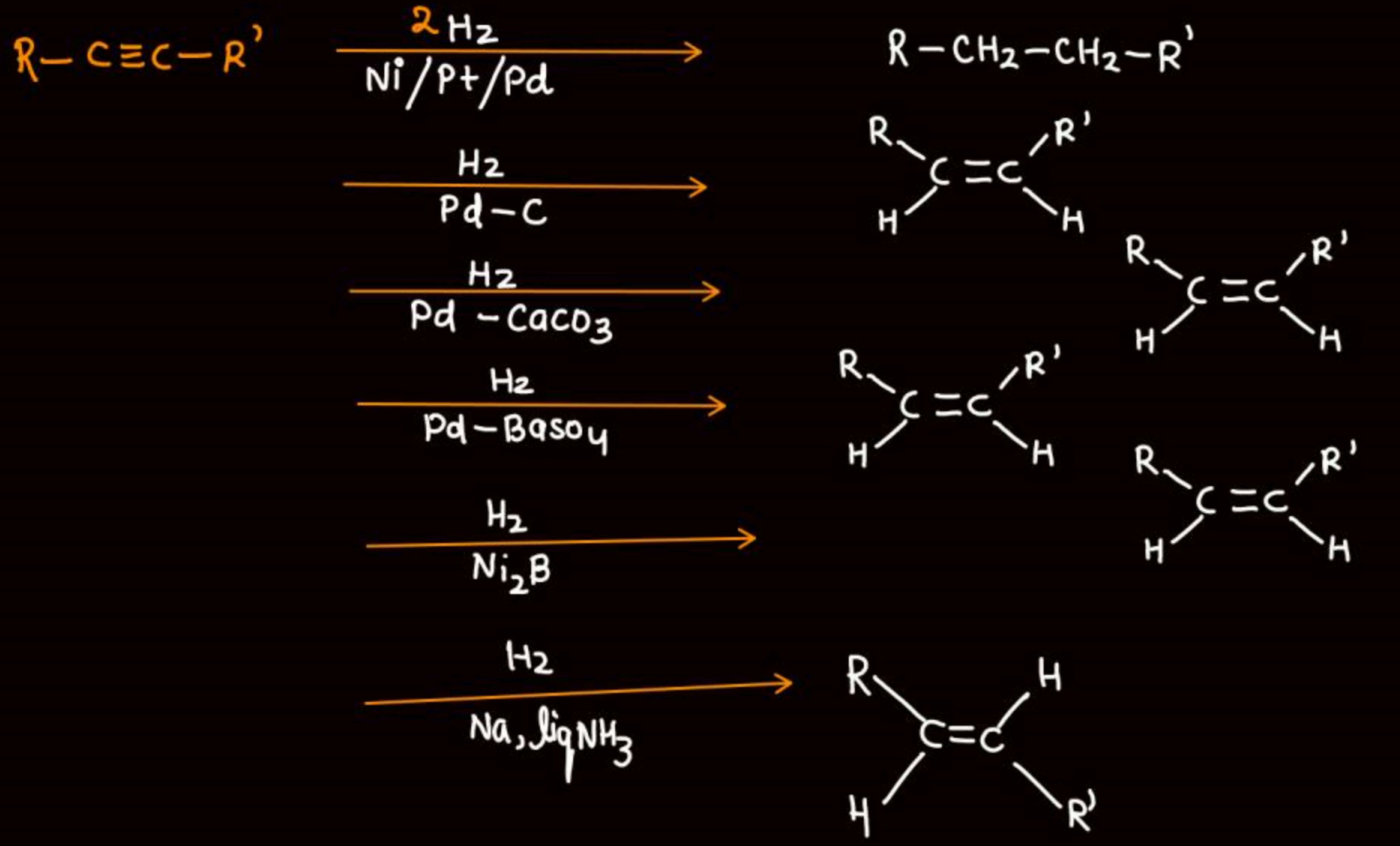
$\xrightarrow[Pd-BaSO_4]{H_2}$ ⟶ Rosenmund catalyst

$\xrightarrow[Ni_2B]{H_2}$ (nickel Boride) ⟶ P_2 Catalyst

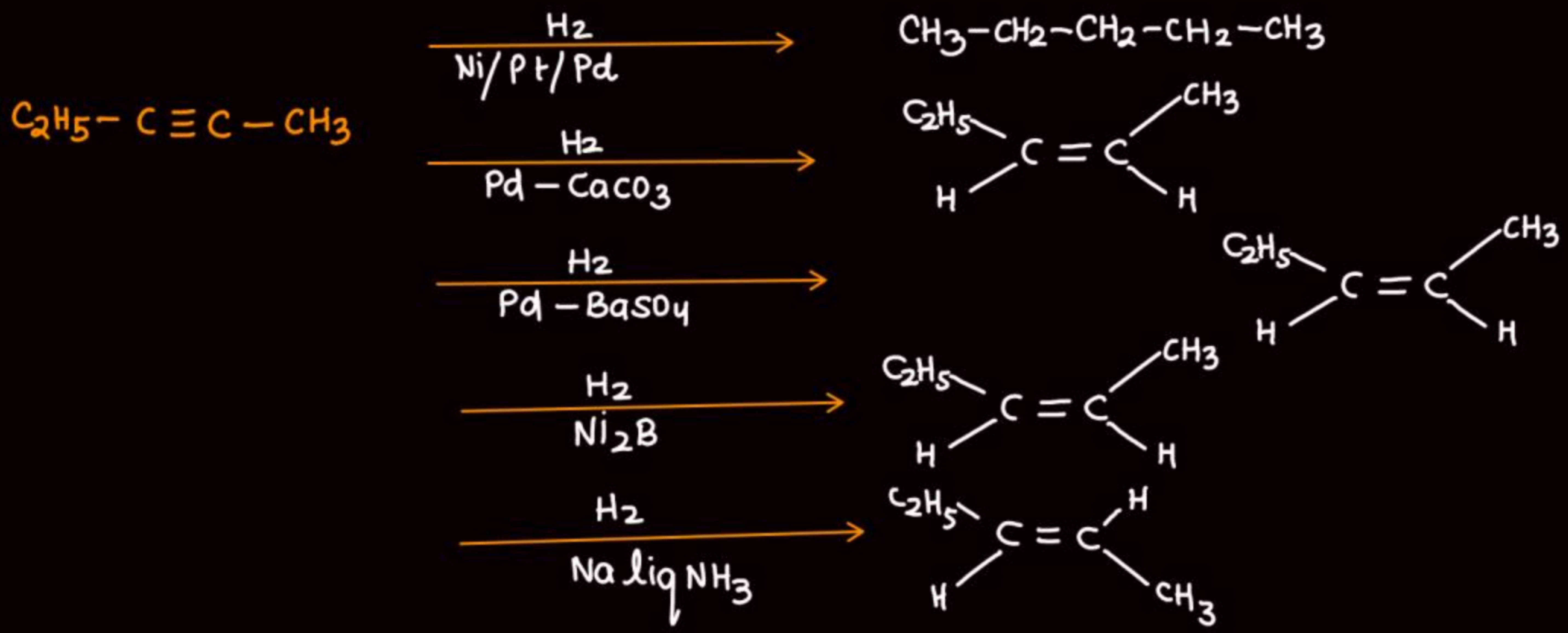
} Syn addition of H_2 ↓ Cys alkene

$\xrightarrow[Na, liq\ NH_3]{H_2}$ ⟶ Birch Reduction

} Anti addition of H_2 ↓ Trans Alkene



R–C≡C–R'
2H2
Ni/Pt/Pd
R–CH2–CH2–R'
H2
Pd–C
H2
Pd–CaCO3
H2
Pd–BaSO4
H2
Ni2B
H2
Na, liq NH3
R
R'
H
C=C



C2H5 − C ≡ C − CH3
H2
Ni/Pt/Pd
CH3−CH2−CH2−CH2−CH3
H2
Pd − CaCO3
C2H5
CH3
C = C
H
H
H2
Pd − BaSO4
C2H5
CH3
C = C
H
H
H2
Ni2B
C2H5
CH3
C = C
H
H
H2
Na liq NH3
C2H5
H
C = C
H
CH3

$CH_3-C\equiv CH$ (Terminal Alkyne)

$$CH_3-C\equiv CH \xrightarrow[Ni/Pt/Pd]{H_2} CH_3-CH_2-CH_3$$

$$\xrightarrow[Pd-C]{H_2} \; (CH_3)(H)C=C(H)(H)$$

$$\xrightarrow[Pd-CaCO_3]{H_2} \; (CH_3)(H)C=C(H)(H)$$

$$\xrightarrow[Pd-BaSO_4]{H_2} \; (CH_3)(H)C=C(H)(H)$$

$$\xrightarrow[Ni_2B]{H_2} \; (CH_3)(H)C=C(H)(H)$$

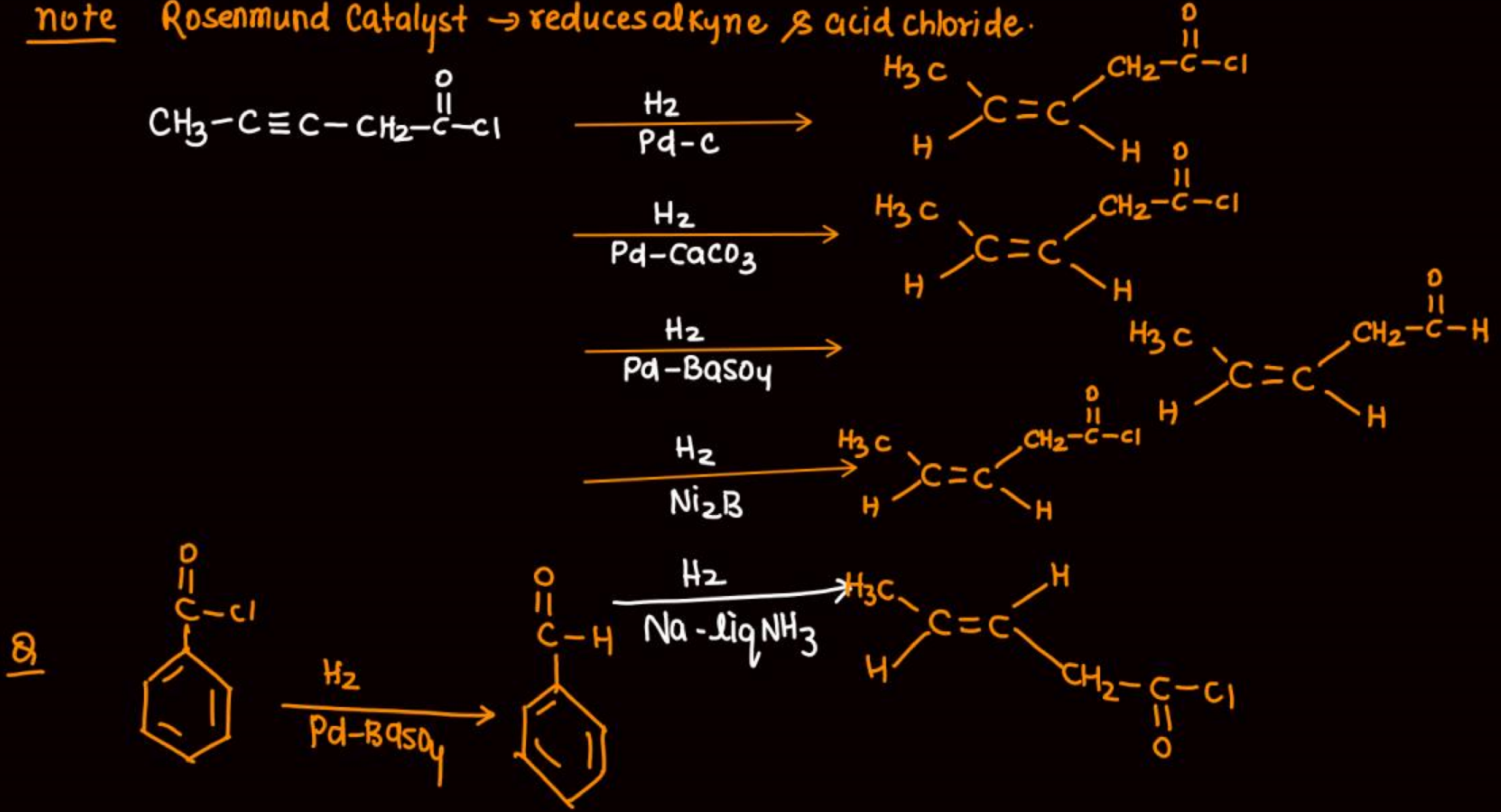
$$\xrightarrow[Na-liq\,NH_3]{H_2} \; CH_3-C\equiv C^{\ominus}Na^{+} + NH_4^{+}$$

(NH_3 ↓ Base)

<u>note</u> → Birch Reduction gives acid–base reaction with terminal alkyne

(Birch Reduction ↓ Base; terminal alkyne ↓ acidic H)

note Rosenmund Catalyst → reduces alkyne & acid chloride.



$R-CH=CH_2$
or
$R-CH=CH-R'$

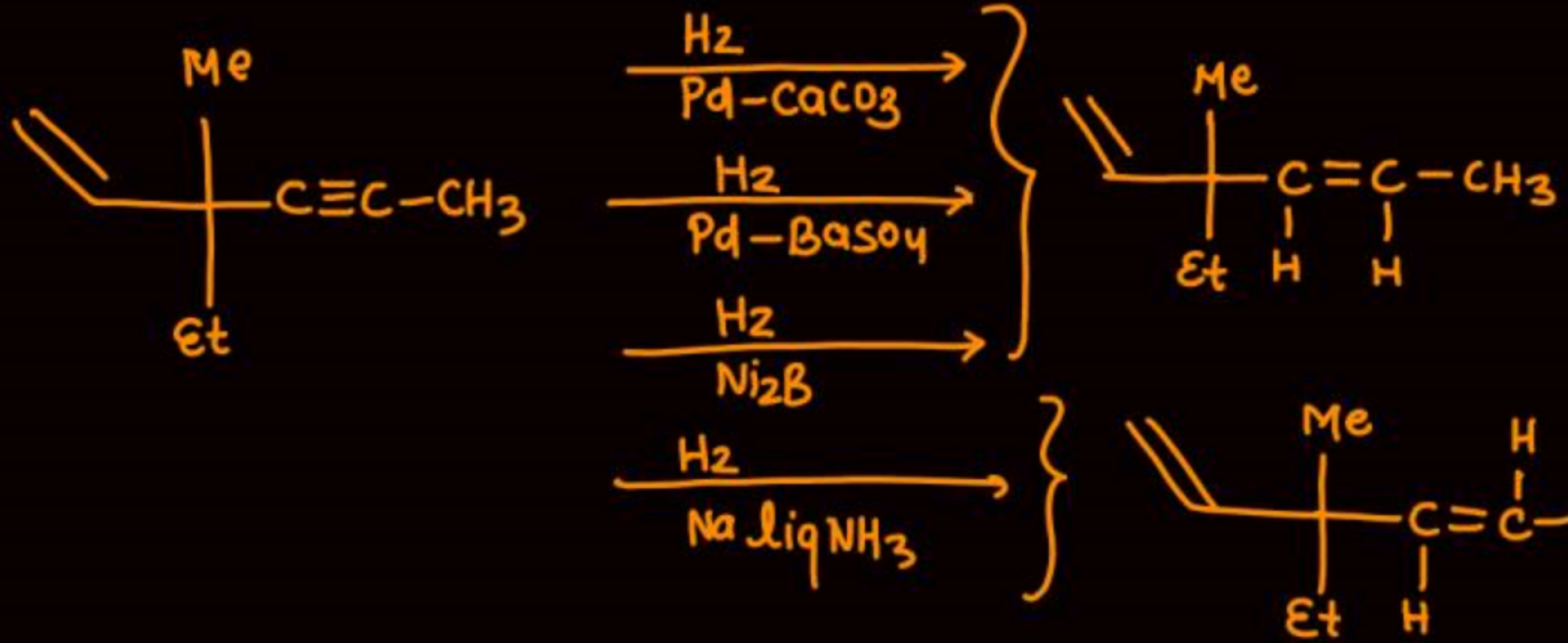
$\xrightarrow[Pd-C]{H_2}$ ×

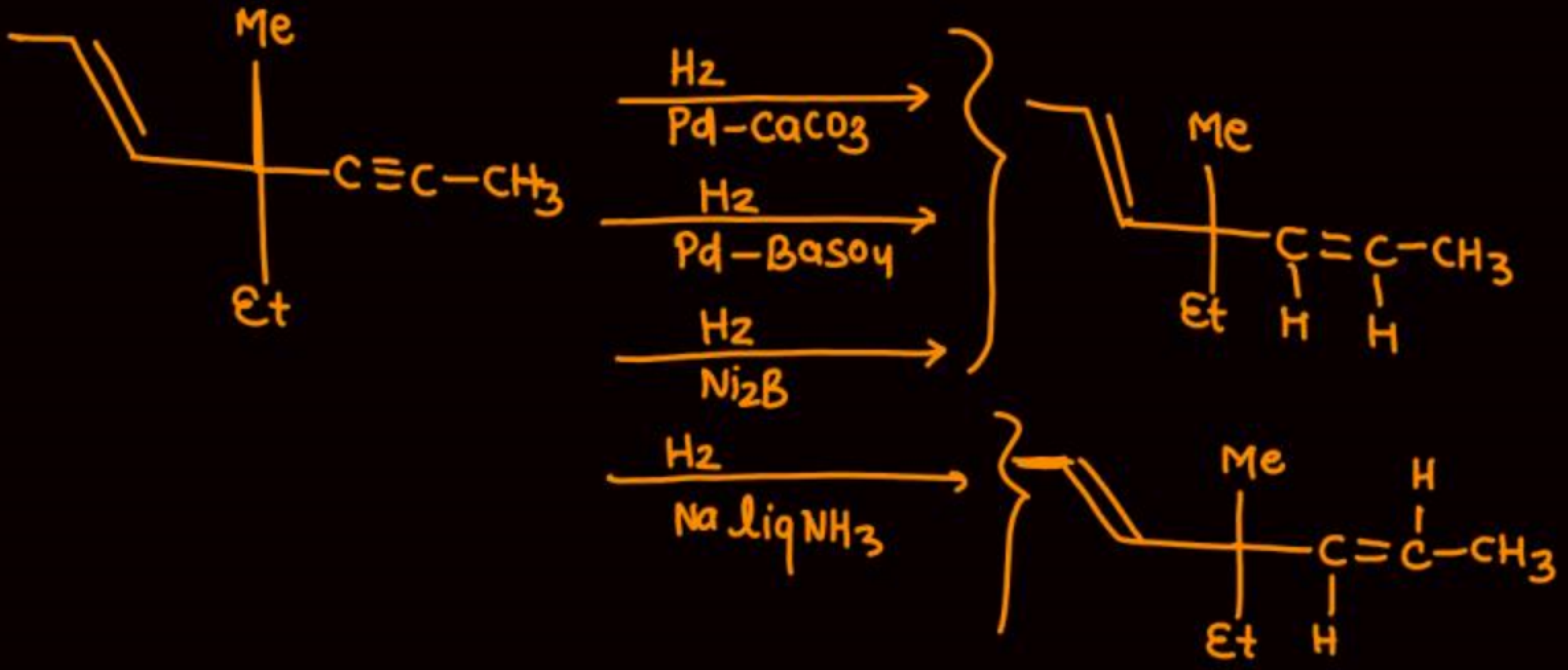
$\xrightarrow[Pd-CaCO_3]{H_2}$ ×

$\xrightarrow[Pd-BaSO_4]{H_2}$ ×

$\xrightarrow[Ni_2B]{H_2}$ ×

$\xrightarrow[Na-liq\ NH_3]{H_2}$ ×





ALKYL HALIDE TO ALKENE

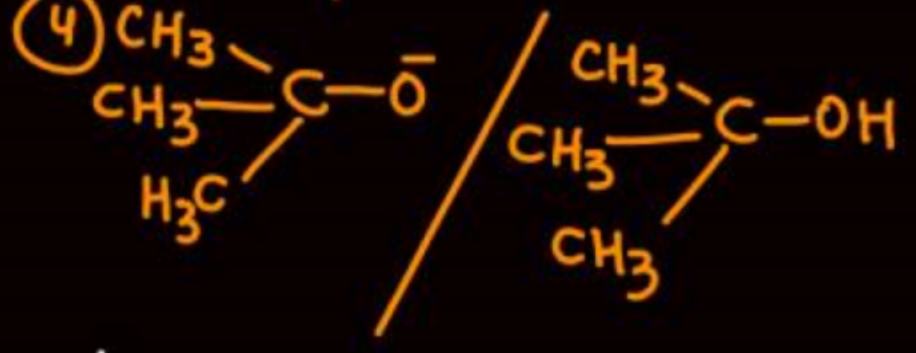
MonoHalide

$R-CH_2-CH_2-X \xrightarrow{\text{① alc KOH}/\Delta \text{ or } NaNH_2/NH_3} R-CH=CH_2 + HX$

② $R-O^-/R-OH$

③ CH_3-O^-/CH_3-OH

④



Strong Base

- DeHydroHalogenation → Removal of HX
- alcoholic KOH → KOH + R-ÖH
- ROH + RÖH → RO^-/ROH (KO^- (strong base))

DiHalide

$R-CH(X)-CH_2(X) \xrightarrow{\text{① Zn-dust}/\Delta} R-CH=CH_2$

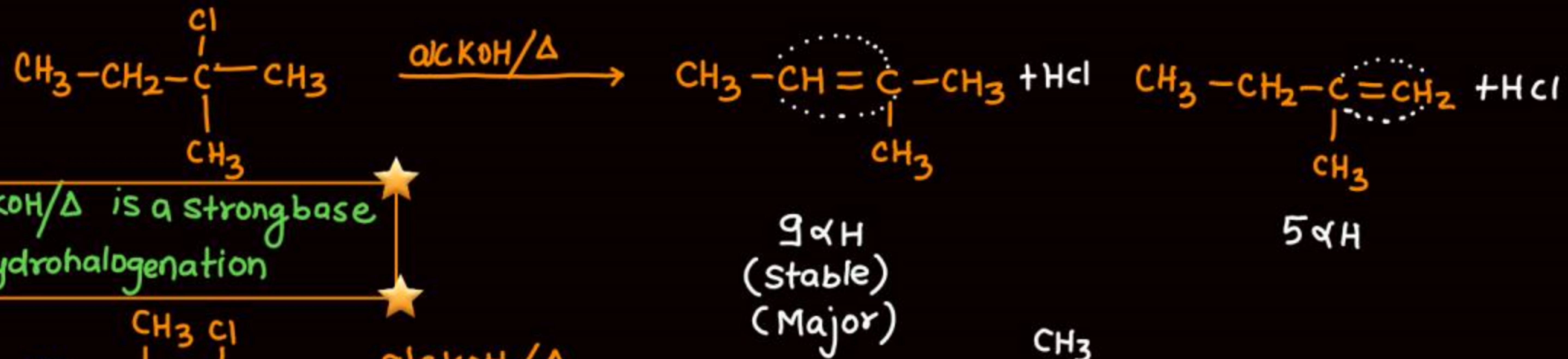
② NaI/acetone

③ Ag-Powder

④ Na-ether

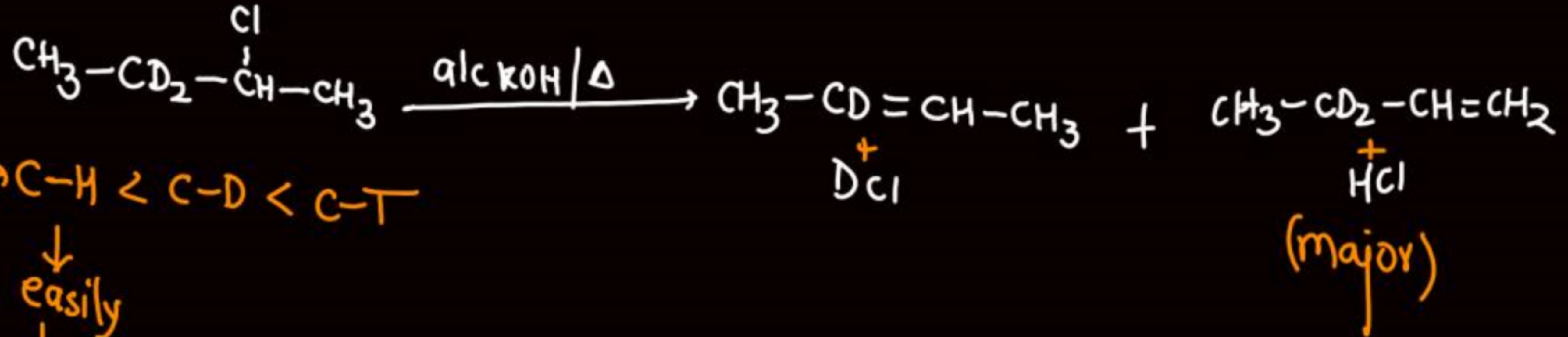
- DeHalogenation → Removal of X_2

Que $CH_3-CH_2-CH_2-Cl \xrightarrow{alc\,KOH/\Delta} CH_3-CH=CH_2 + HCl$

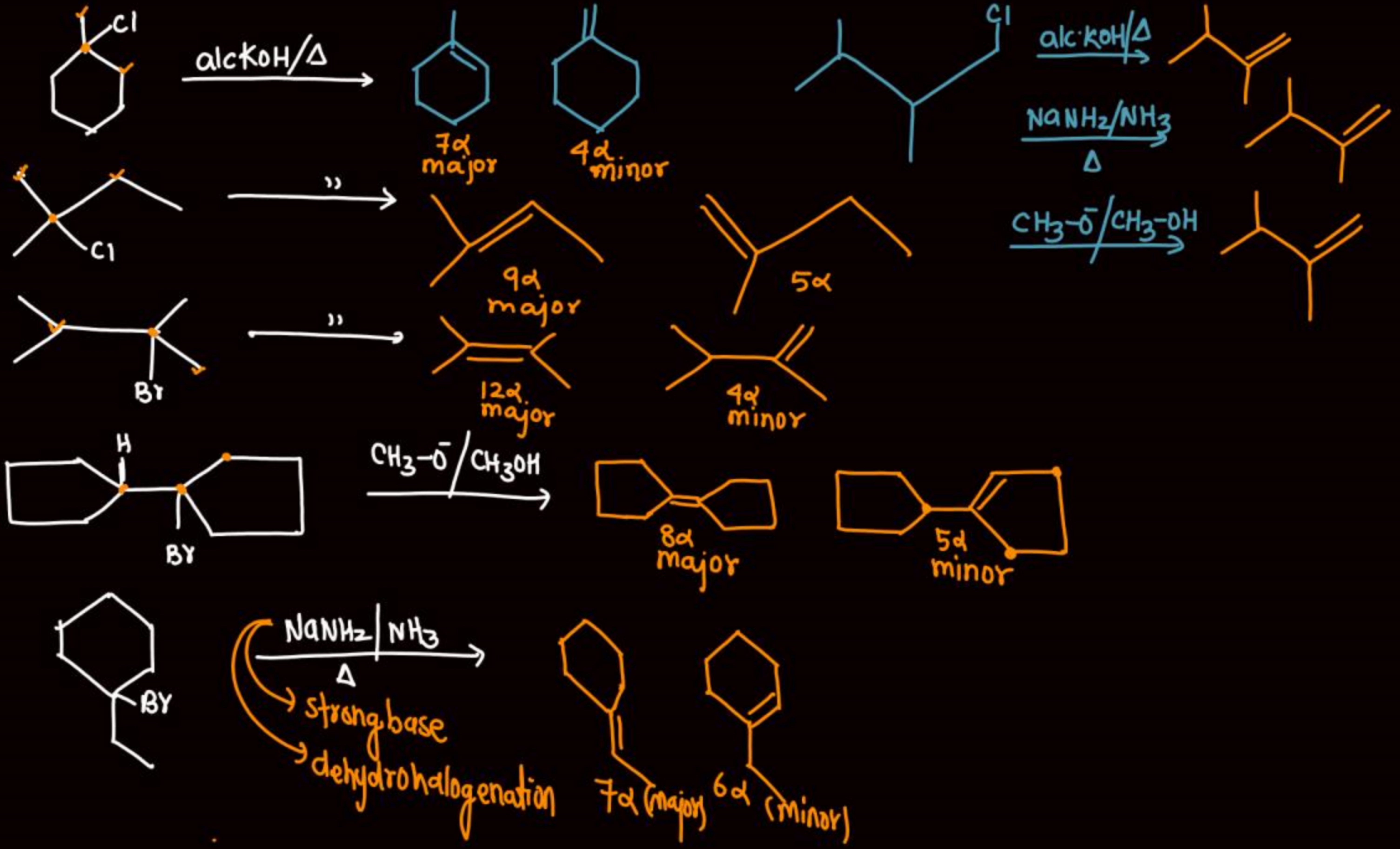


> **note** → alc KOH/Δ is a strong base
> dehydrohalogenation





Bond strength → C–H < C–D < C–T
↓
easily break



Cl
alcKOH/Δ
7α major
4α minor
Cl
alc·KOH/Δ
NaNH2/NH3 Δ
CH3-O⁻/CH3-OH
Cl
"
9α major
5α
Br
"
12α major
4α minor
H
Br
CH3-O⁻/CH3OH
8α major
5α minor
Br
NaNH2/NH3 Δ
strong base
dehydrohalogenation
7α (major)
6α (minor)

note → Bulky Base (→ tert-butoxide) gives Hoffman Product as major product.

→ ______ attacks on less hindered Hydrogen.

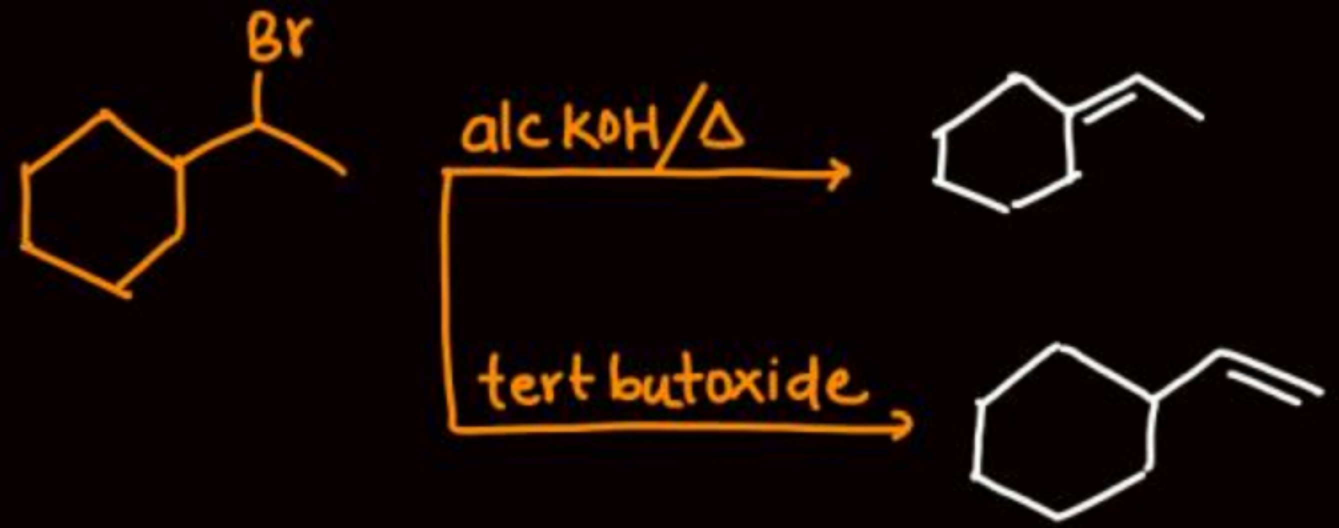
$$CH_3-CH_2-\underset{}{\overset{Cl}{\overset{|}{C}H}}-CH_3 \xrightarrow[\Delta]{\text{alc KOH / NaNH}_2\text{, NH}_3\text{ / RO}^-\text{/ROH}}$$

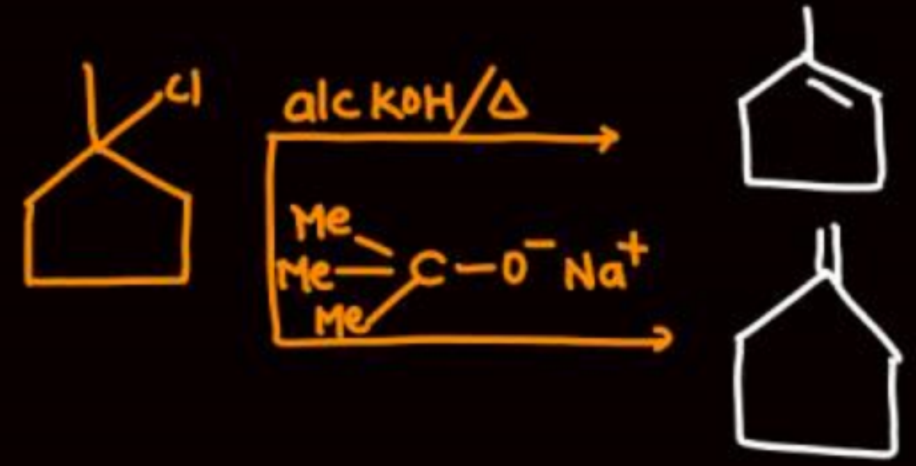
$CH_3-CH=CH-CH_3$	$CH_3-CH_2-CH=CH_2$
Major	Minor
6αH	2αH
Saytzeff Prod	Hoffman product

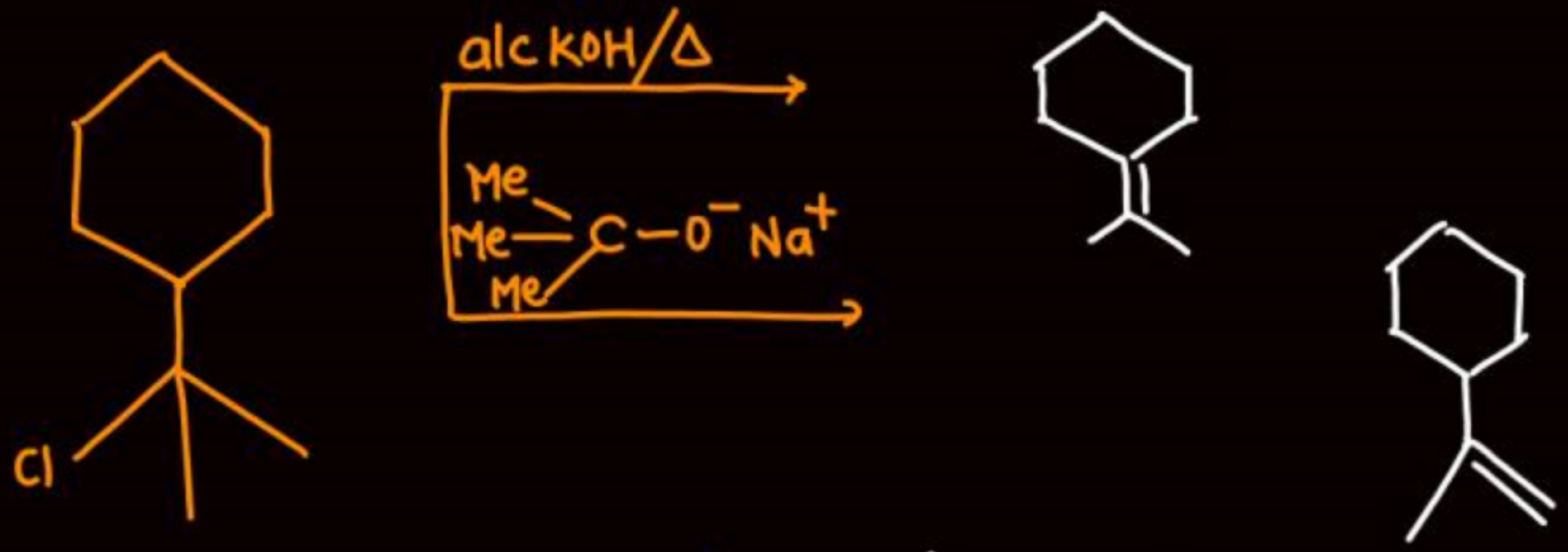
$$CH_3-CH_2-\underset{}{\overset{Cl}{\overset{|}{C}H}}-CH_3 \xrightarrow{(CH_3)_3C-O^-}$$

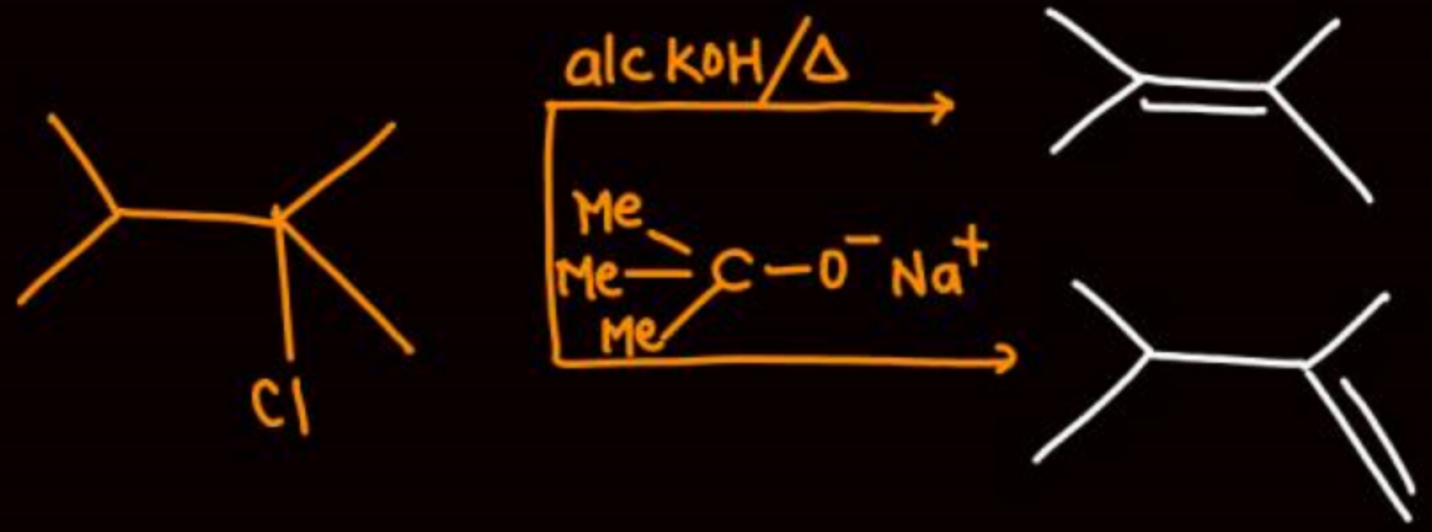
$CH_3-CH_2-CH=CH_2$	$CH_3-CH=CH-CH_3$
Major	Minor
Hoffman prod	6αH
	Saytzeff Prod

Q Write Major Prod.









Alcohol ⟶ Alkene

alcohol + acid → OH हटाओ
Cation बनाओ
alkene बनाओ

$$CH_2-CH_2\ (H,\ OH) \xrightarrow{-H_2O} CH_2=CH_2$$

- Dehydration Reaction (Removal of H_2O)
- Elimination Reaction

• Conc H_2SO_4
• Conc H_3PO_4
• Al_2O_3

- Intermediate → Carbocation
- Rate of Reaction ∝ stability of Carbocation.

Que Compare rate of dehydration reaction

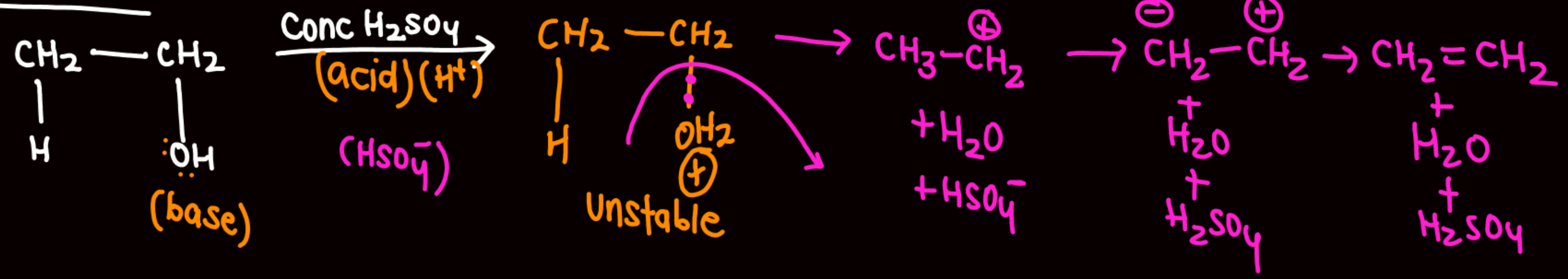
ⓐ $CH_3-C(CH_3)_2-OH$

ⓑ $CH_3-CH(CH_3)-OH$

ⓒ CH_3-CH_2-OH

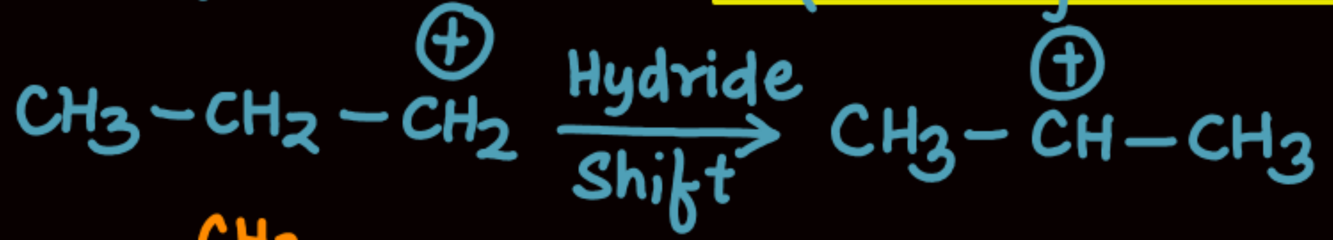
rate: a > b > c

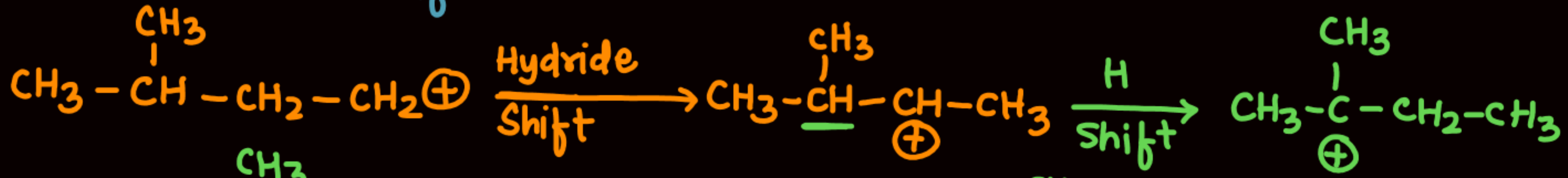
Mechanism :-

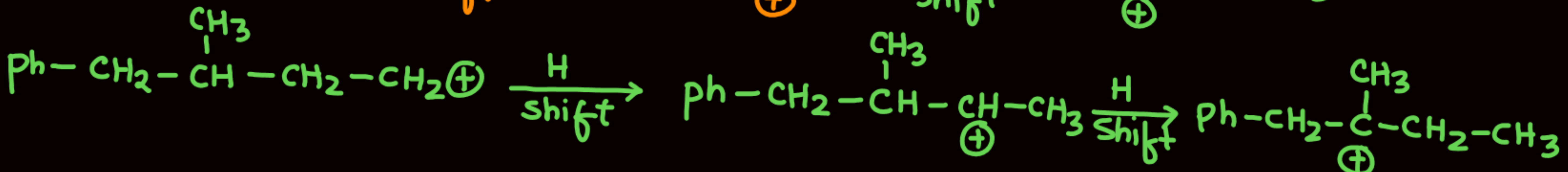


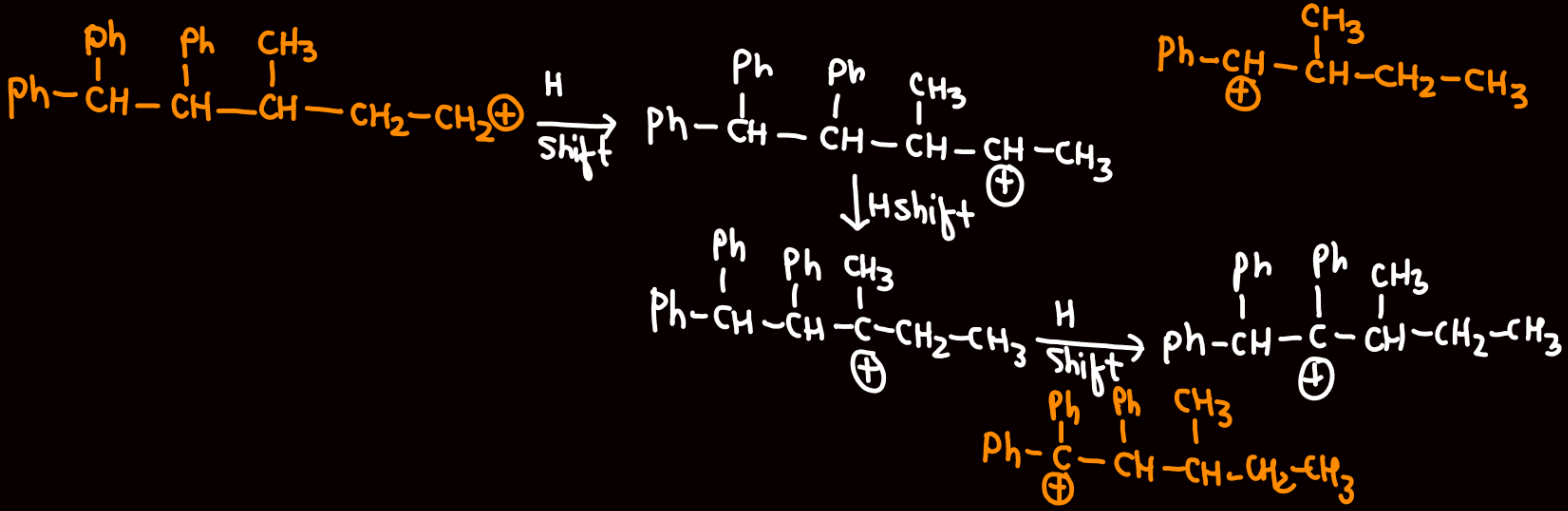
Shifting of Carbocation

Rearrangement of Carbocation

①


②


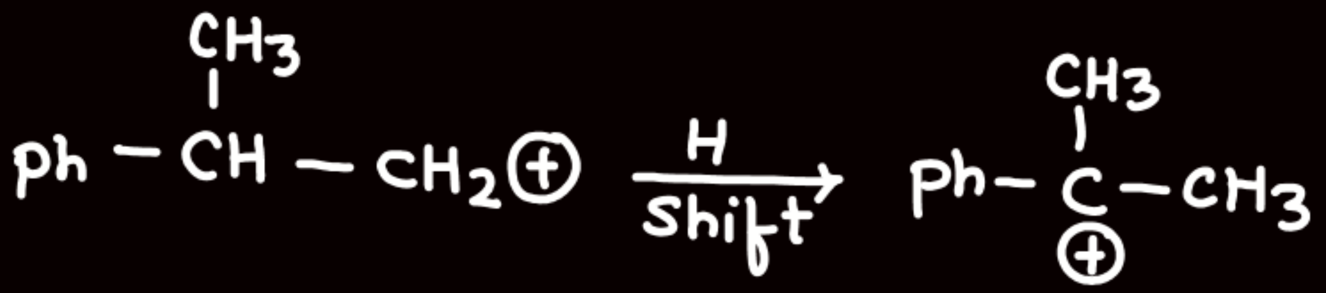
③


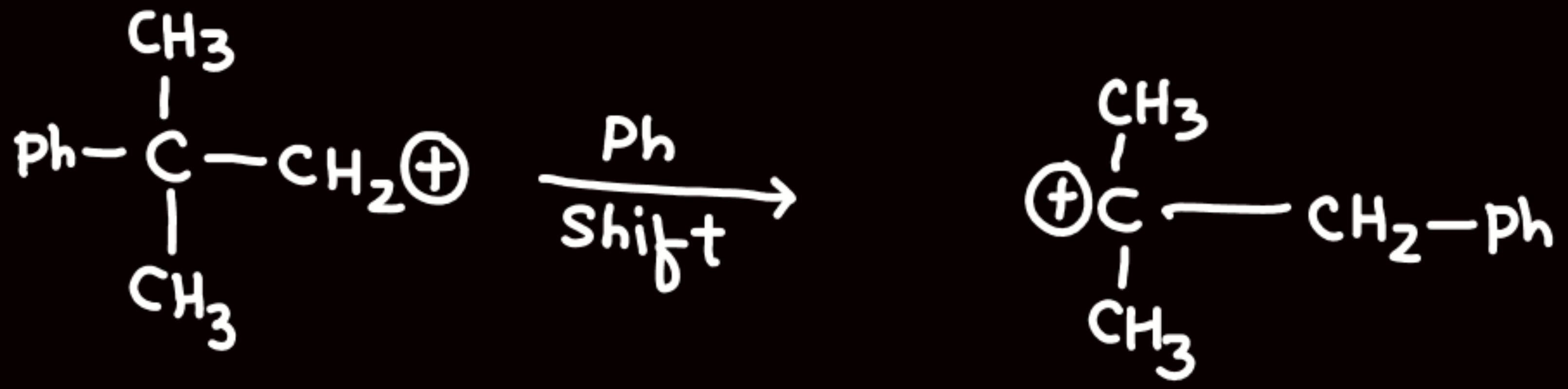
④


Ways of Shifting of Carbocation

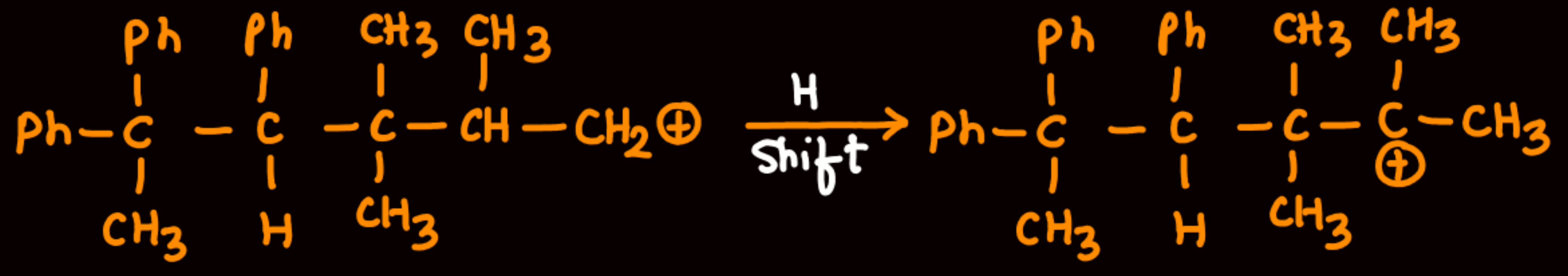
1. Hydride shift.
2. phenyl shift.
3. Methyl shift.

Priority → H shift > Ph shift > Me shift

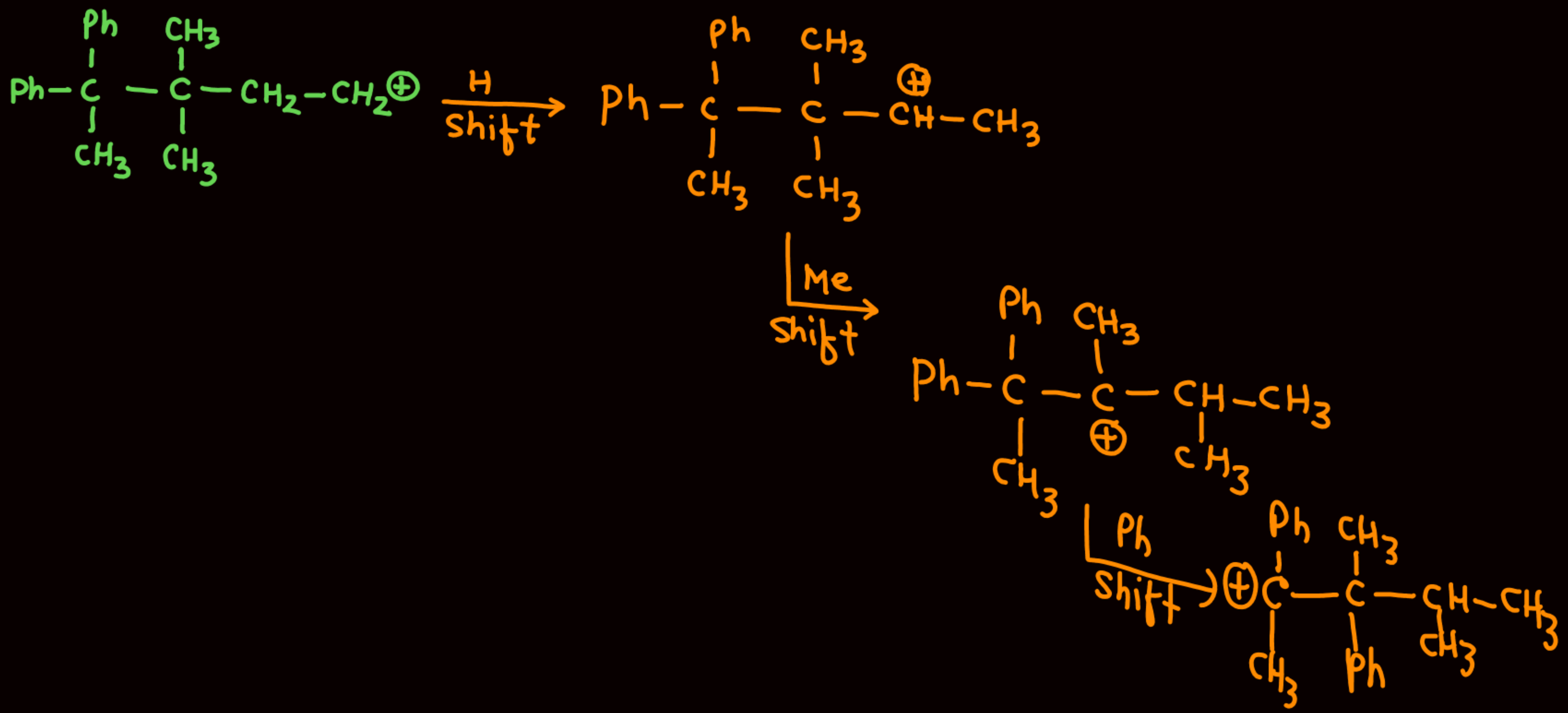








पड़ोसी से shifting करना है।
Shifting तभी होगा
जब stability बढ़ेगा



VTcity

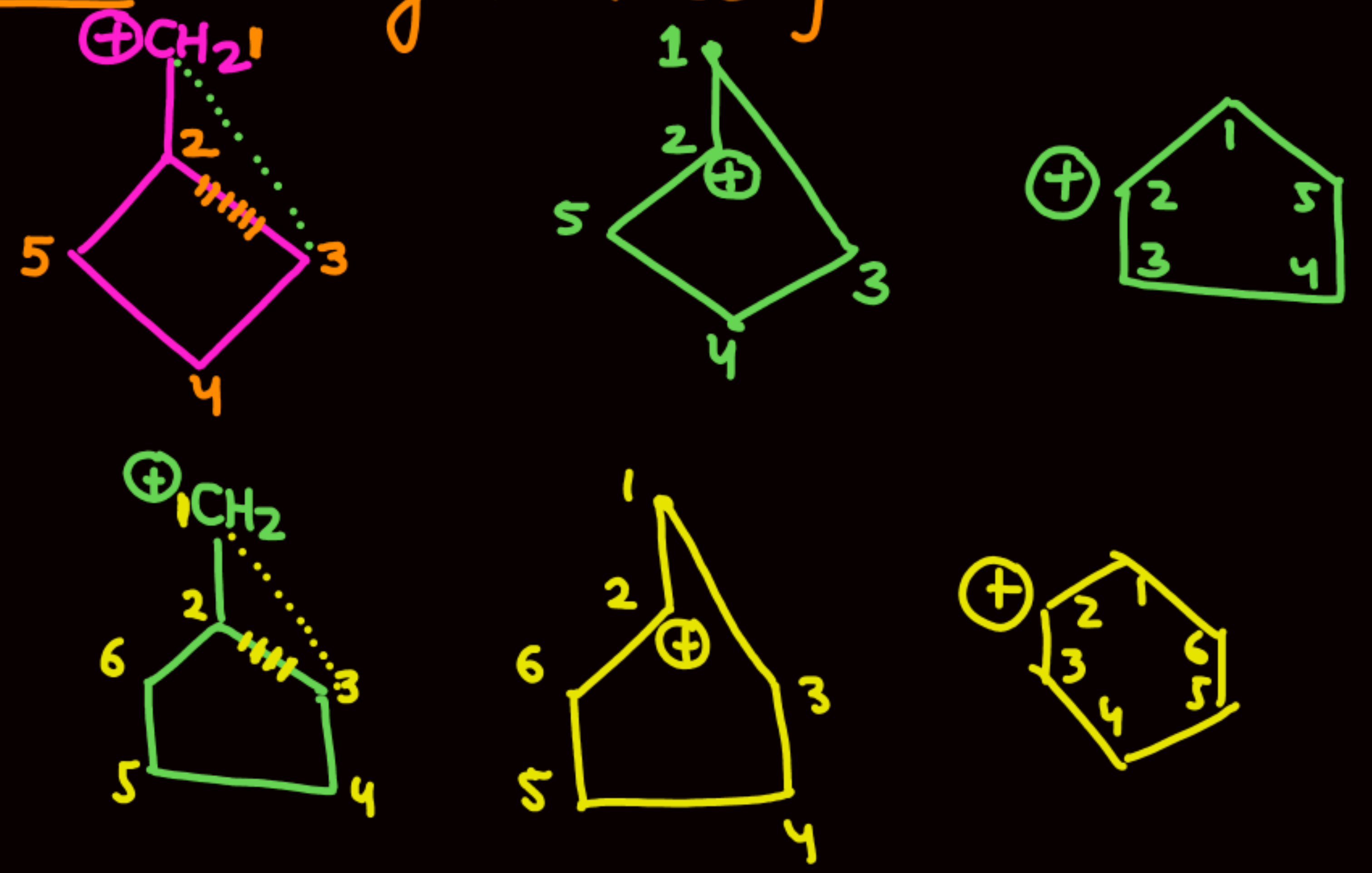
Ring Expansion & Ring Contraction

Ring Expansion

4 member Ring $\xrightarrow{\text{Expand}}$ 5 member Ring $\xrightarrow{\text{Expand}}$ 6 member Ring

- → 2, 3 का bond break.
- → 1, 3 का bond Form.
- → 1 का Charge 2 पर

Cond 1 → Ring से directly attatch atom पर +ve charge होना चाहिए

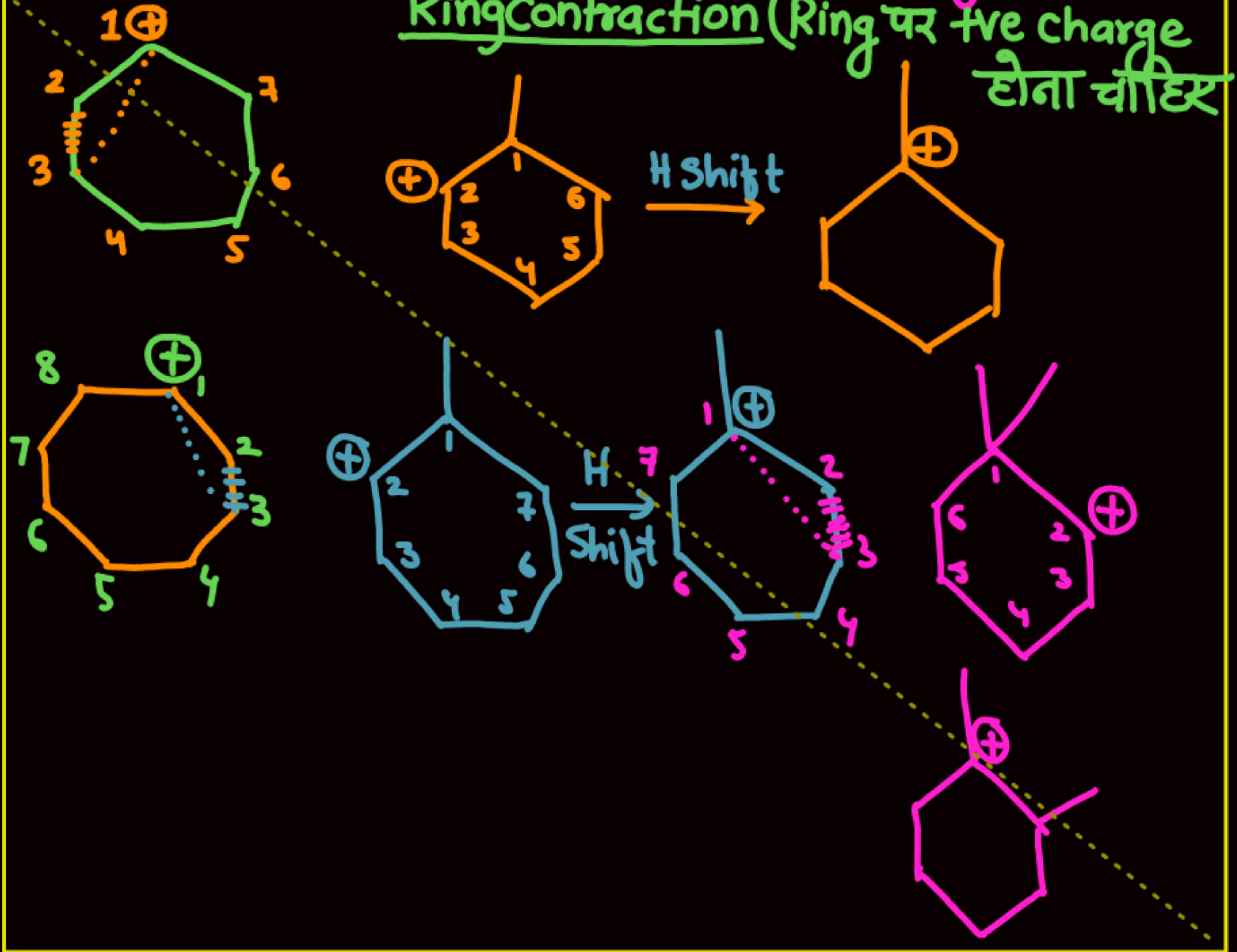




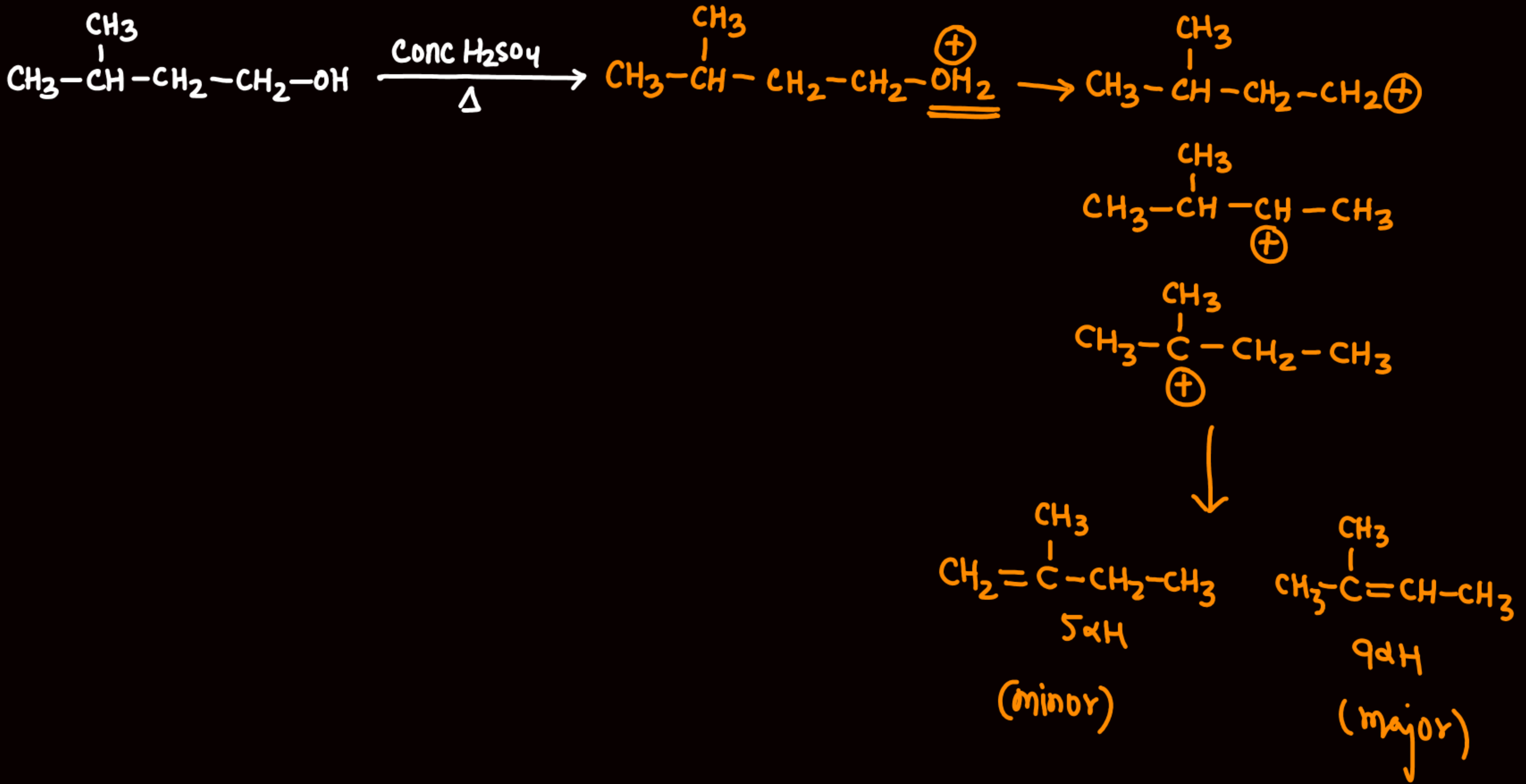
→ no Expansion

CpM cation
dancing Resonance

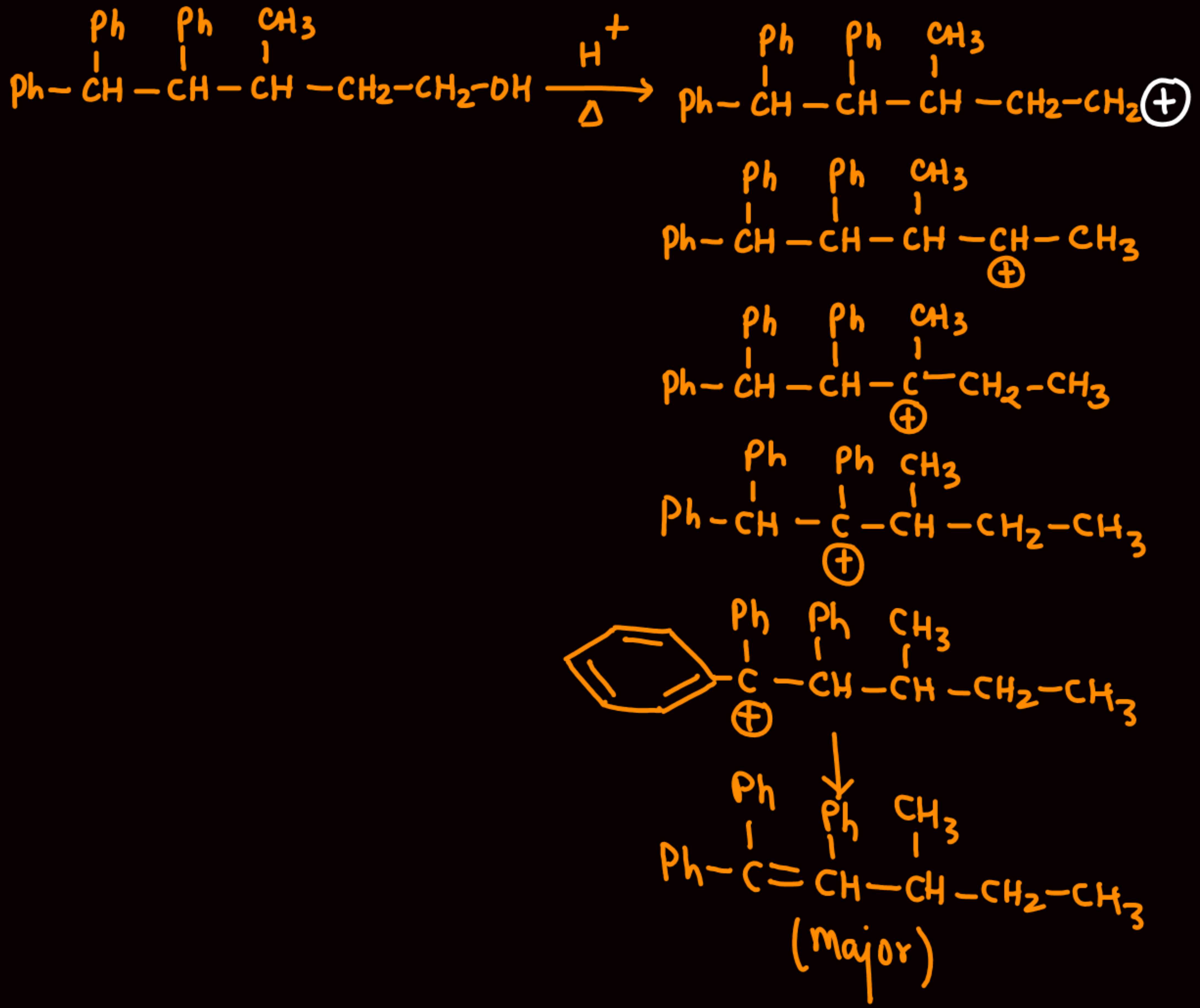
Ring contraction (Ring पर +ve charge होना चाहिए)

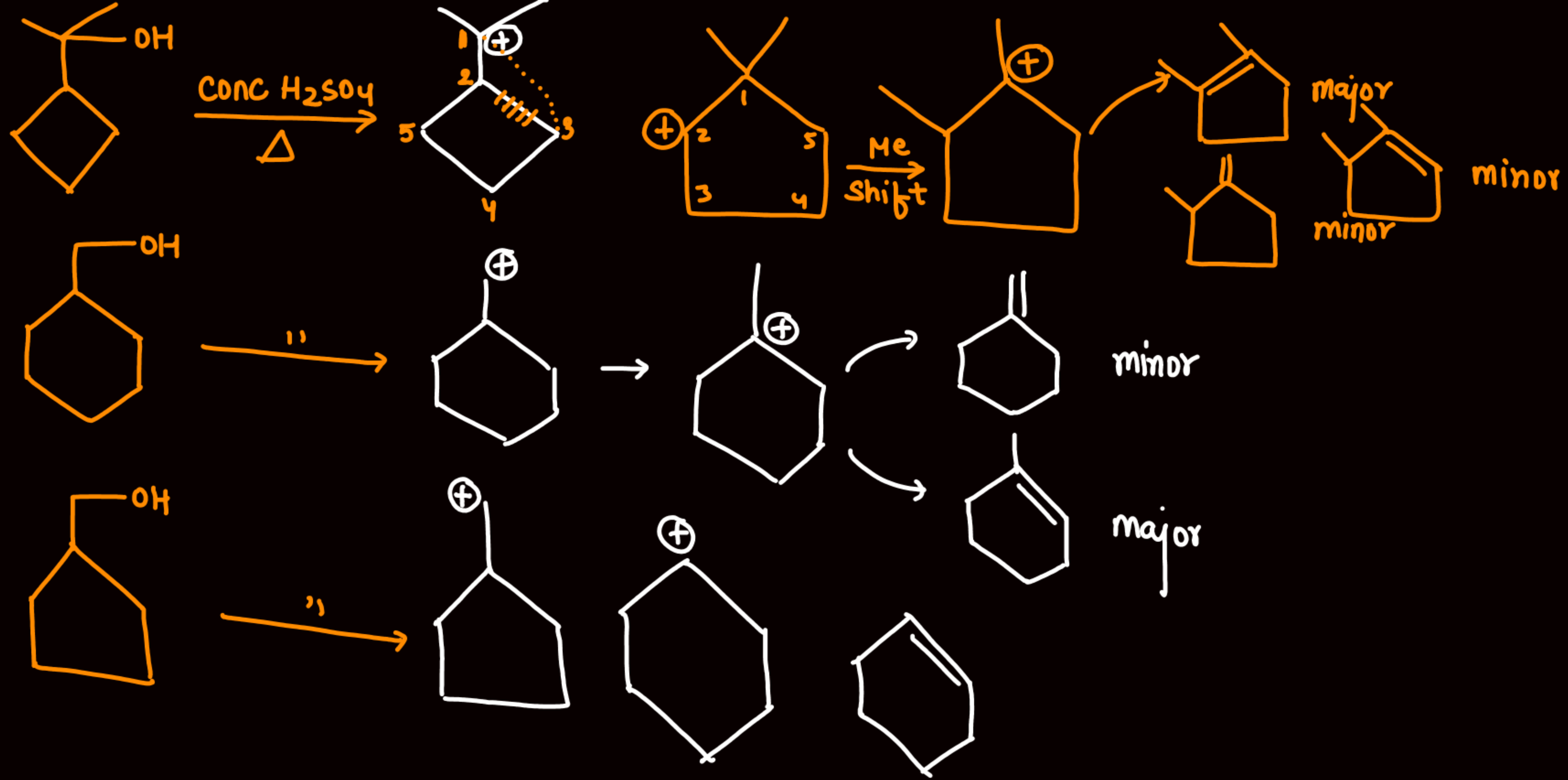


2018


CH3-CH(CH3)-CH2-CH2-OH
Conc H2SO4
Δ
CH3-CH(CH3)-CH2-CH2-OH2(+)
CH3-CH(CH3)-CH2-CH2(+)
CH3-CH(CH3)-CH(+)-CH3
CH3-C(+)(CH3)-CH2-CH3
CH2=C(CH3)-CH2-CH3
5αH
(minor)
CH3-C(CH3)=CH-CH3
9αH
(major)

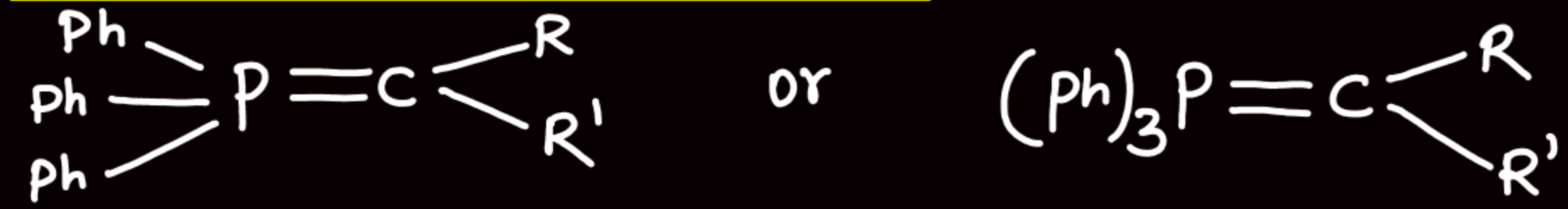
2019

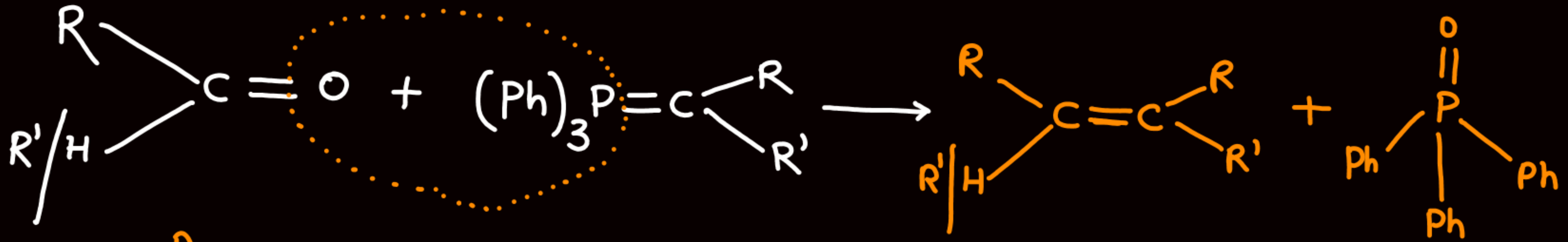


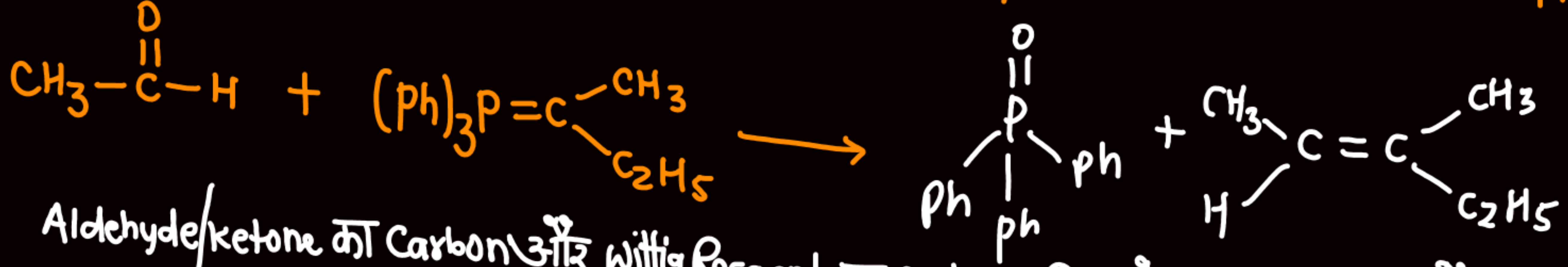

OH
conc H2SO4
Δ
Me shift
major
minor
minor
OH
minor
major
OH

aldehyde/ketone ⟶ alkene

① wittig Reagent







VTST Aldehyde/ketone का Carbon और wittig Reagent का carbon मिलाके Alkene बनता है। phosphorous oxygen से Bond बनाता है।

Carboxylic acid → alkene (PPCH)   Kolbe's electrolysis

$CH_3^{\cdot}$

$CH_3^{\cdot}$

$$\begin{matrix} CH_3-\overset{O}{\overset{\|}{C}}-O^-\,Na^+ + OH-H \\ CH_3-\underset{O}{\underset{\|}{C}}-O^-\,Na^+ + OH-H \end{matrix} \xrightarrow{\text{electrolysis}} \underbrace{CH_3-CH_3 + 2CO_2}_{\text{Anode}} + \underbrace{2NaOH + H_2}_{\text{Cathode}}$$

$$\begin{matrix} CH_2-\overset{O}{\overset{\|}{C}}-O^-\,Na^+ + OH-H \\ | \\ CH_2-\underset{O}{\underset{\|}{C}}-O^-\,Na^+ + OH-H \end{matrix} \xrightarrow{\text{electrolysis}} \underbrace{CH_2=CH_2 + 2CO_2}_{\text{anode}} + \underbrace{2NaOH + H_2}_{\text{cathode}}$$

$$\begin{matrix} CH-\overset{O}{\overset{\|}{C}}-O^-\,Na^+ + OH-H \\ \| \\ CH-\underset{O}{\underset{\|}{C}}-O^-\,Na^+ + OH-H \end{matrix} \xrightarrow{\text{''}} \underbrace{CH\equiv CH + 2CO_2}_{\text{anode}} + \underbrace{2NaOH + H_2}_{\text{cathode}}$$

Ester – alkene

$$R-\overset{O}{\overset{\|}{C}}-O-R' \xrightarrow{\text{liq } N_2 \text{ \& glass wool}}$$

$R-\overset{O}{\overset{\|}{C}}-O-$: Forms Carboxyllic acid

R' : Forms alkene

Q

$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 \xrightarrow{\text{liq } N_2\text{, glass wool}} CH_2=CH_2 + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Q

$$C_2H_5-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3 \xrightarrow{\text{liq } N_2\text{, glass wool}} CH_3-CH=CH_2 + C_2H_5-\overset{O}{\overset{\|}{C}}-OH$$

Chemical Reaction of Alkene

$>C \overset{\pi}{=} C<$ → weak pi bond & breaks easily [Nucleophilic in nature]

So, characteristic reaction of alkene is electrophilic addition reaction.

Electrophilic addition reaction of alkene

(i) addition of H_2 (Catalytic Hydrogenation) (PPCH)
(ii) addition of HX (Hydrohalogenation)
(iii) addition of H_2O (Hydration)
(iv) addition of HOX
(v) addition of X_2
(vi) addition of H_2SO_4
(vii) Hydroformylation reaction

Addition of H_2 on alkene

$$CH_3-CH=CH_2 \xrightarrow[Ni/Pt/Pd]{H_2} \underset{\displaystyle H}{\underset{|}{CH_3-CH}}-\underset{\displaystyle H}{\underset{|}{CH_2}}$$

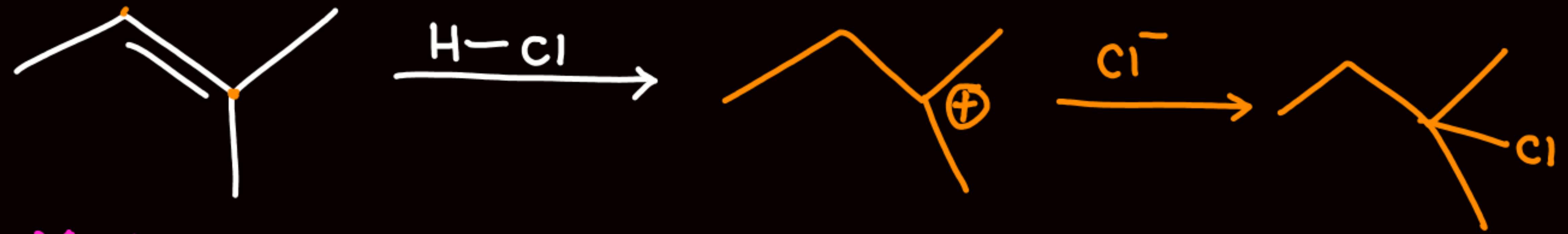
- Syn addition of H_2
- H_2 gas gets adsorbed on metal surface.
- H_2/Ni (300-500°c) High Temp & High Pressure {Sabatier & Sanderen's Reaction}
- H_2/Pt or Pd (Room temp)

Addition of HX on alkene

$$CH_2 = CH_2 \xrightarrow{\overset{\delta+}{H} - \overset{\delta-}{X}} CH_3 - \overset{\oplus}{C}H_2 \xrightarrow{X^{\ominus}} CH_3 - CH_2 - X$$

$$CH_3 - CH = CH_2 \xrightarrow{\overset{\delta+}{H} - \overset{\delta-}{X}} CH_3 - \underset{\oplus}{C}H - CH_3 \xrightarrow{X^{\ominus}} CH_3 - \underset{X}{\underset{|}{C}H} - CH_3$$ (Markovnikov Rule)

$$CH_3 - CH = CH - CH_3 \xrightarrow{H - X} CH_3 - \underset{\oplus}{C}H - CH_2 - CH_3 \xrightarrow{X^-} CH_3 - \underset{X}{\underset{|}{C}H} - CH_2 - CH_3$$

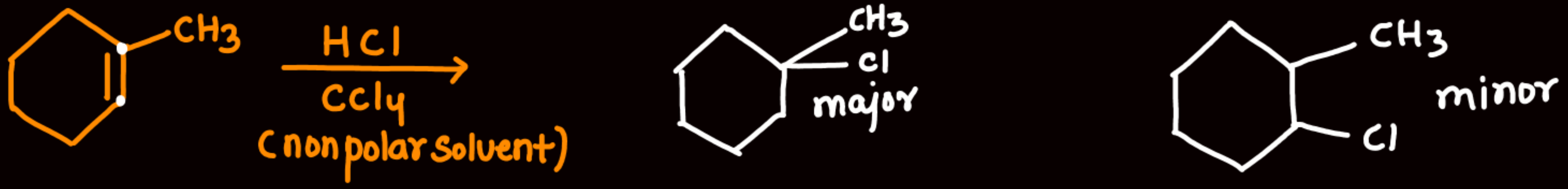


(Markovnikov Rule)

Markovnikov Rule → −ve parts adds to that Carbon where Hydrogen is less.

Anti Markovnikov Rule → −ve parts adds to that Carbon where Hydrogen is More.

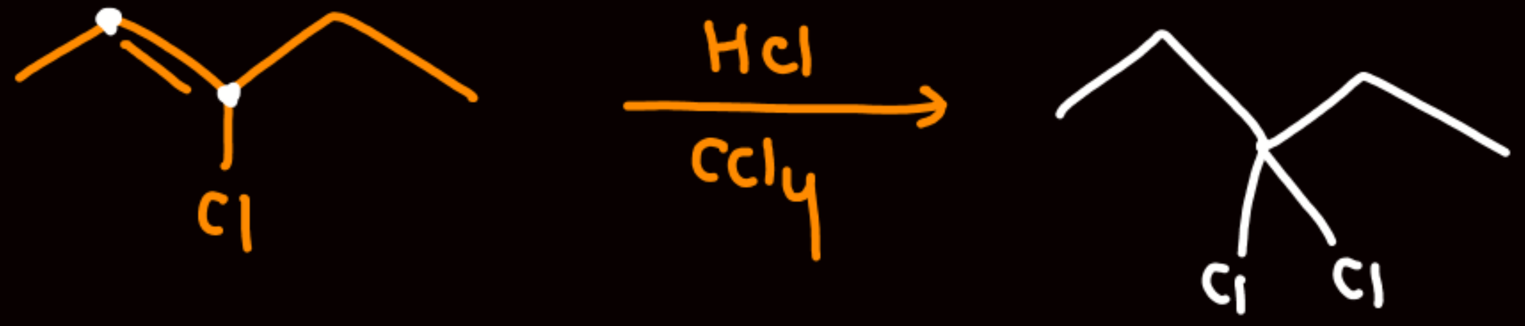
note → nonpolar solvent is used.



$$CH_3-CH=CH-CH_2-CH_3 \xrightarrow[CCl_4]{HBr} CH_3-\overset{\oplus}{CH}-CH_2-CH_2-CH_3\ (5\alpha H) \rightarrow CH_3-\underset{Br}{CH}-CH_2-CH_2-CH_3 \text{ (major)}$$

$$CH_3-CH_2-\overset{\oplus}{CH}-CH_2-CH_3\ (4\alpha H) \rightarrow CH_3-CH_2-\underset{Br}{CH}-CH_2-CH_3 \text{ (minor)}$$





$$Ph-CH=CH-CH_3 \xrightarrow[CCl_4]{HBr} Ph-\overset{\oplus}{CH}-CH_2-CH_3 \rightarrow Ph-\underset{Br}{CH}-CH_2-CH_3 \text{ (major)}$$

$$Ph-CH_2-\overset{\oplus}{CH}-CH_3 \rightarrow Ph-CH_2-\underset{Br}{CH}-CH_3 \text{ (minor)}$$

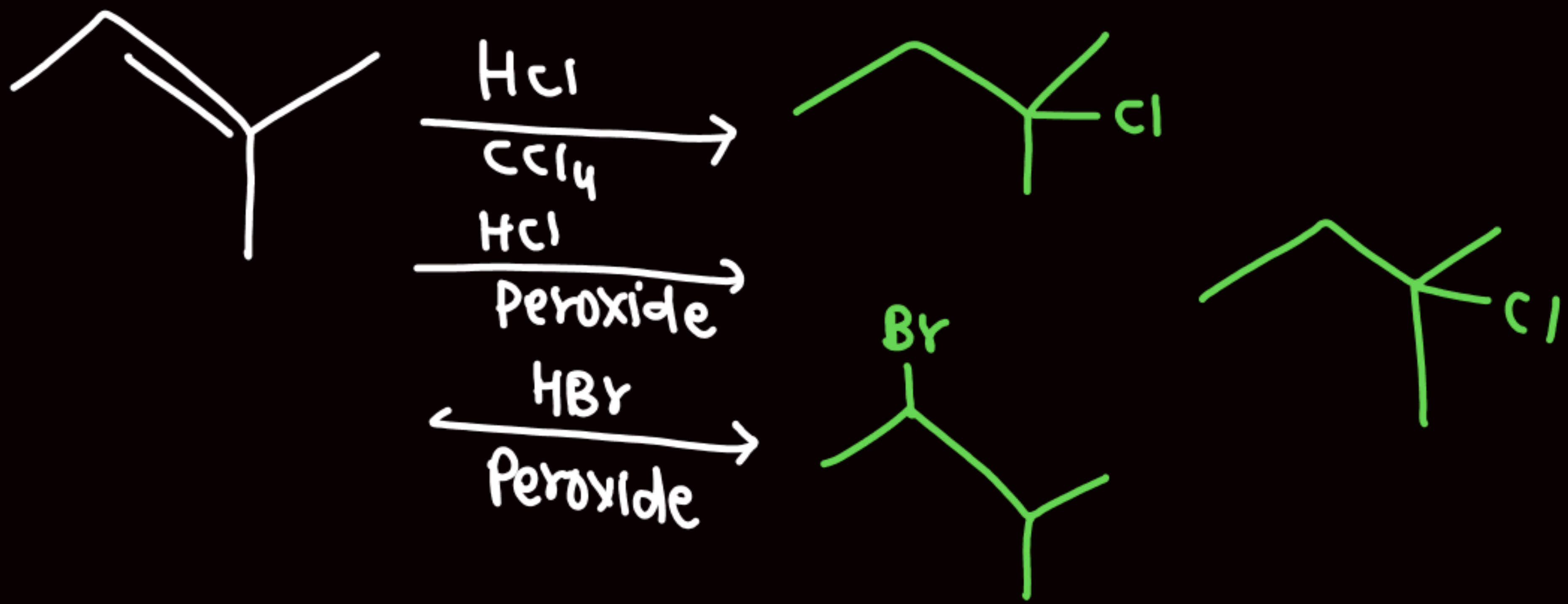
Que $Ph-CH=CH-CH_3 \xrightarrow[CCl_4]{DCl} Ph-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{D}{|}}{CH}-CH_3$

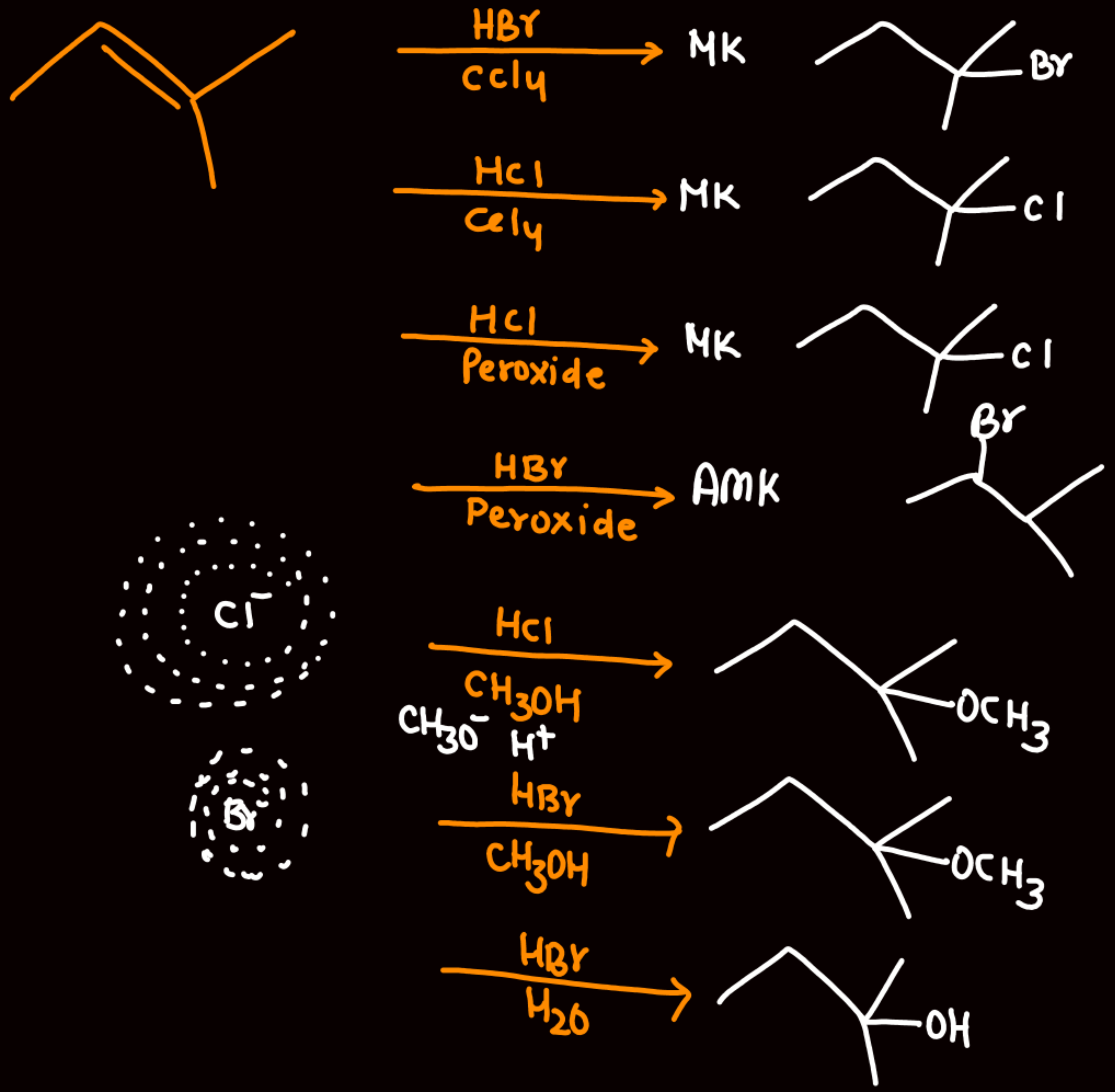
Note → $\xrightarrow[\text{Peroxide}]{HBr}$ Antimarkovnikov Rule gives major product

Que $CH_3-CH=CH_2 \xrightarrow[CCl_4]{HBr} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$ (Markovnikov Rule)

$\xrightarrow[\text{Peroxide}]{HBr} CH_3-CH_2-CH_2-Br$ (Antimarkovnikov Rule)

Que




HBr
ccl4
MK
Br
Hcl
Cel4
MK
cl
Hcl
Peroxide
MK
cl
HBr
Peroxide
AMK
Br
Cl⁻
Hcl
CH3OH
OCH3
CH3O⁻ H+
Br
HBr
CH3OH
OCH3
HBr
H2O
OH

HX addition on conjugated diene

$$CH_2=CH-CH=CH_2 \xrightarrow[CCl_4]{HBr}$$ High Temp ($40^\circ C$) → 1,4 addition prod is formed.

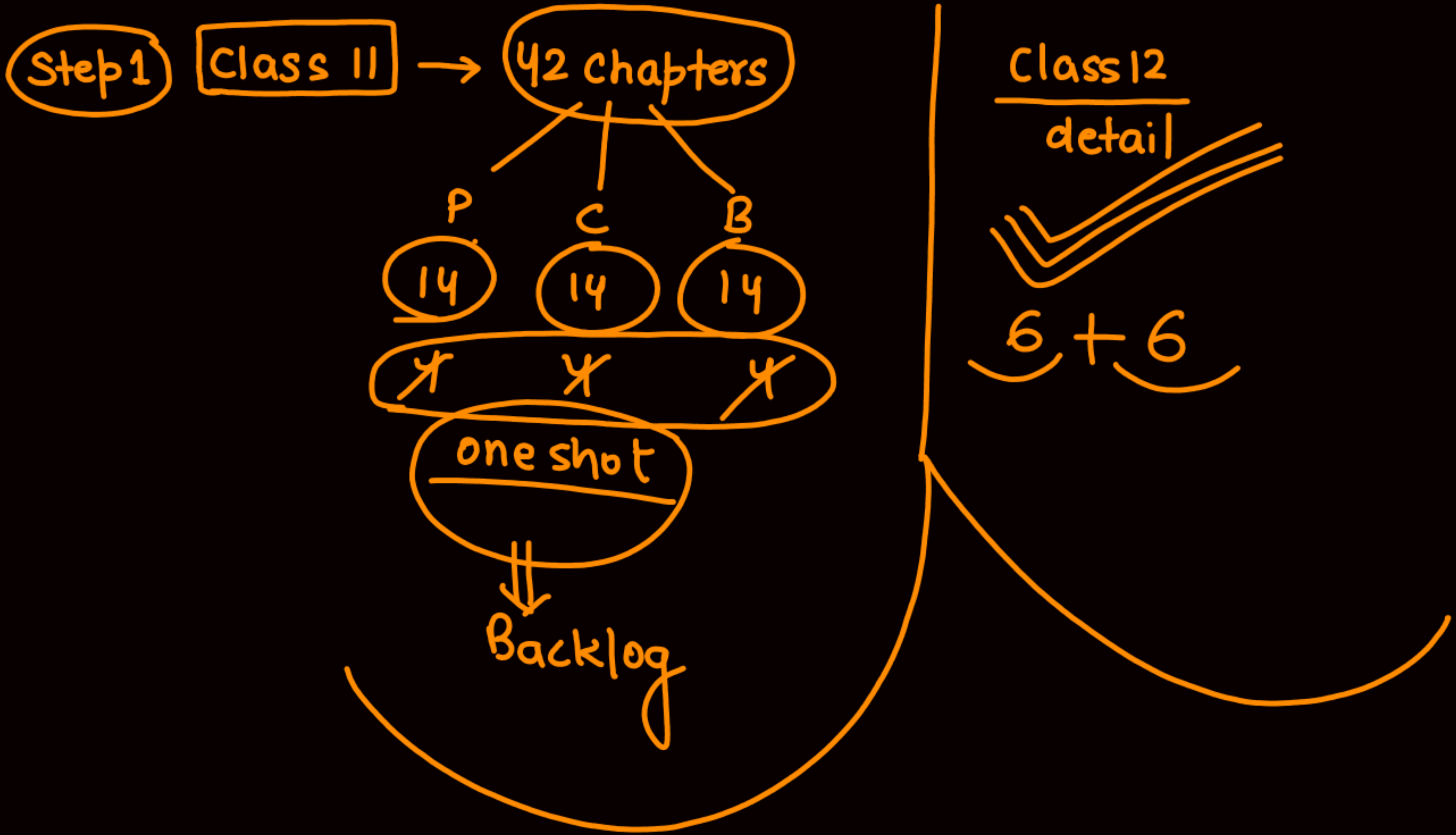
Low Temp ($-25^\circ C$) → 1,2 addition prod is formed.

$$\underset{1}{CH_2}=\underset{2}{CH}-\underset{3}{CH}=\underset{4}{CH_2} \xrightarrow[CCl_4\,(40^\circ C)]{HCl} CH_2(H)-CH_2-CH_2-CH_2(Cl)$$

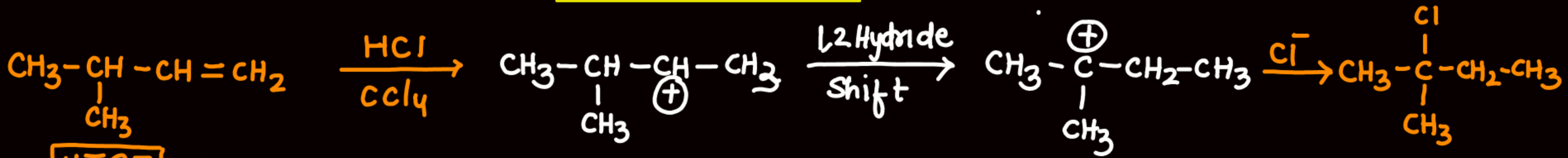
$$\xrightarrow[CCl_4\,(-25^\circ C)]{HCl} CH_2=CH-CH(Cl)-CH_2(H)$$

$$CH_3-CH=CH-CH=CH-CH_3 \xrightarrow[CCl_4]{HCl\ (Low\ Temp)} CH_3-CH=CH-CH(H)-CH(Cl)-CH_3$$

$$\xrightarrow[CCl_4]{HBr\ (High\ Temp)} CH_3-CH(H)-CH_2-CH_2-CH(Br)-CH_3$$

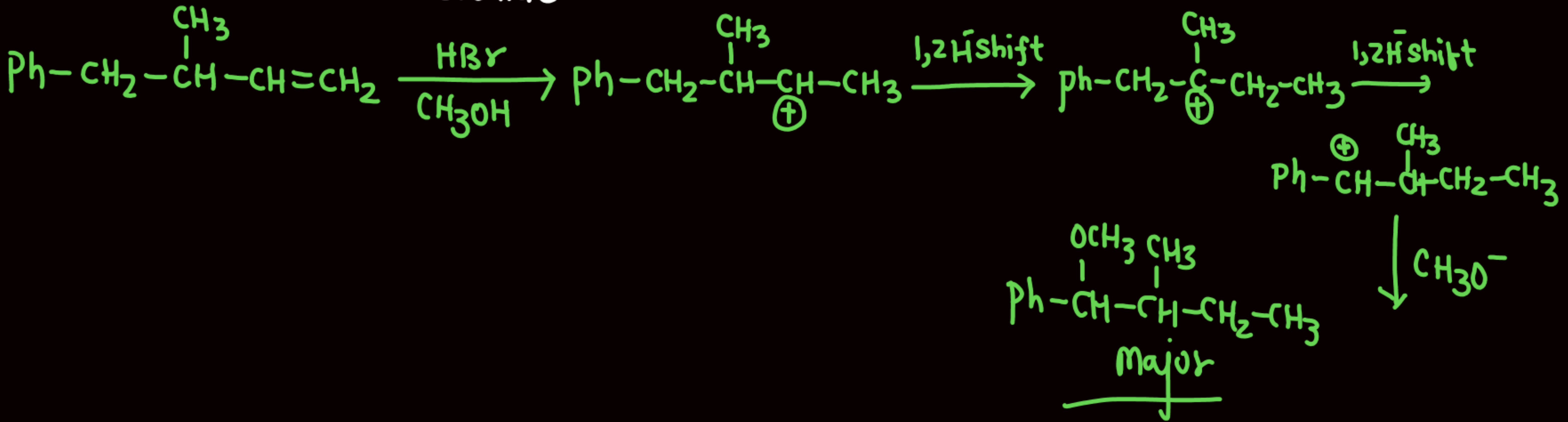

Step 1
Class 11
42 chapters
P
C
B
14
14
14
4
4
4
one shot
Backlog
Class 12
detail
6 + 6

addition of HX

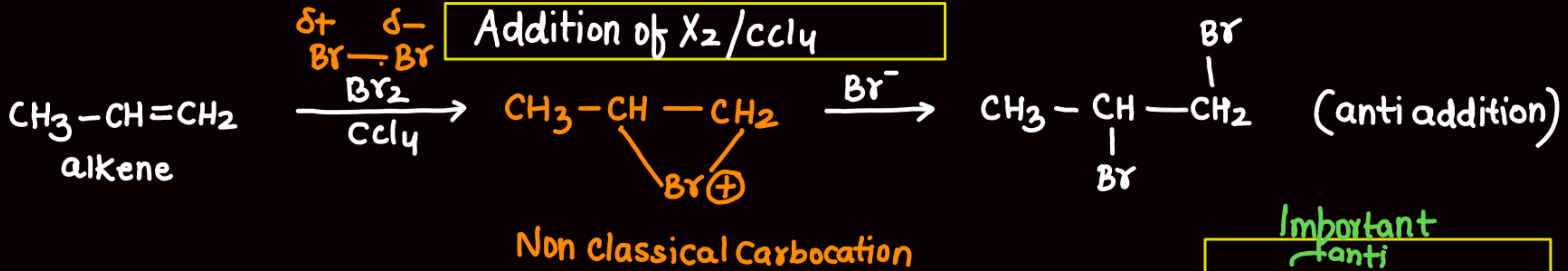


VTST Stable Carbocation
↓
Rearrangement
↓
X^- attack



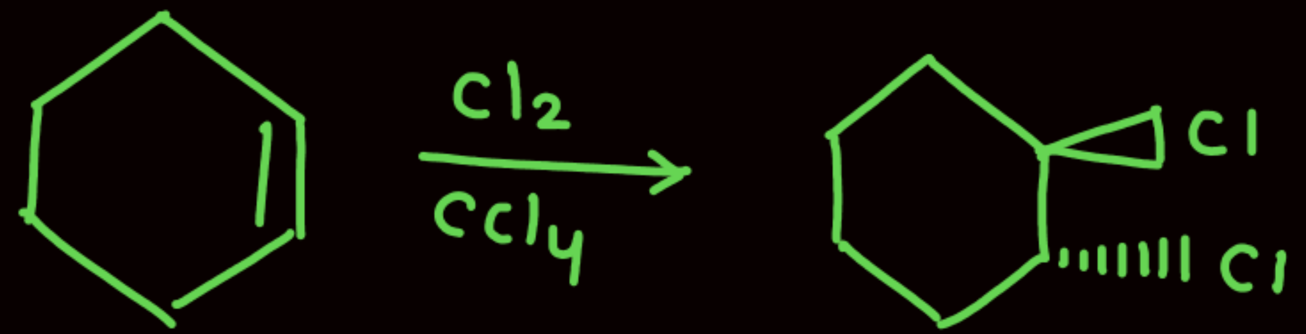


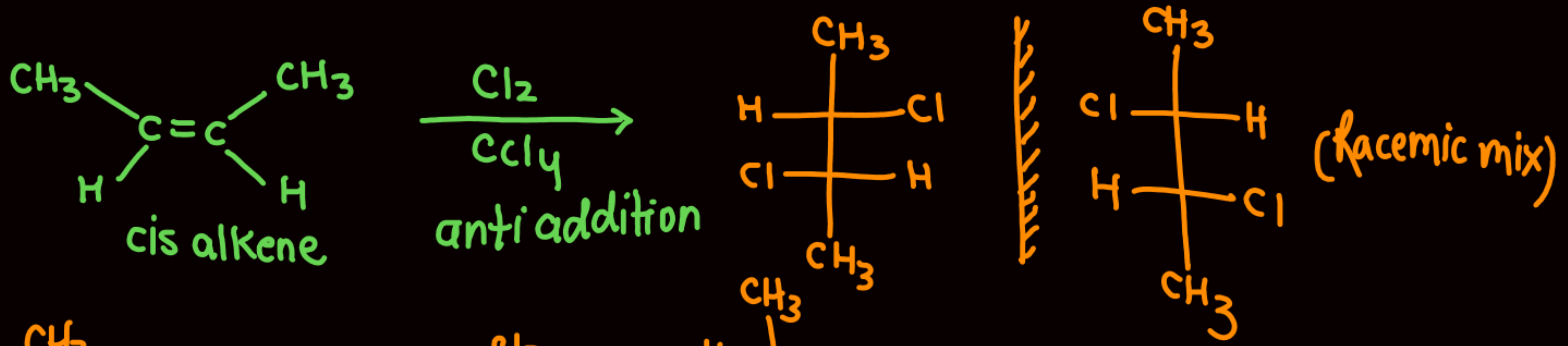
Addition of X_2/CCl_4

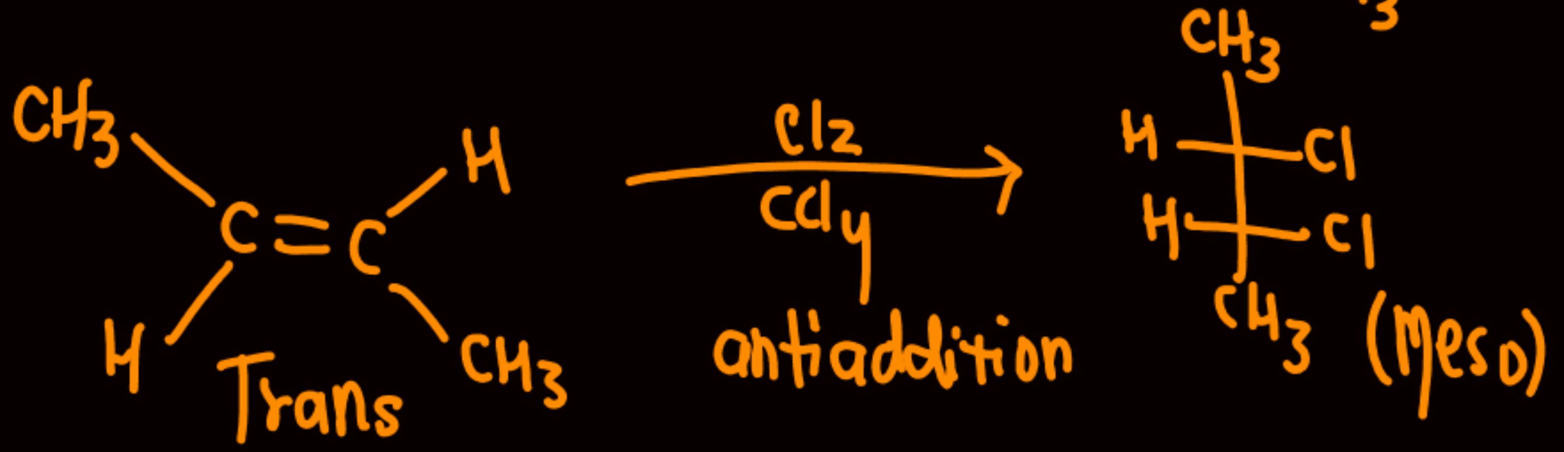


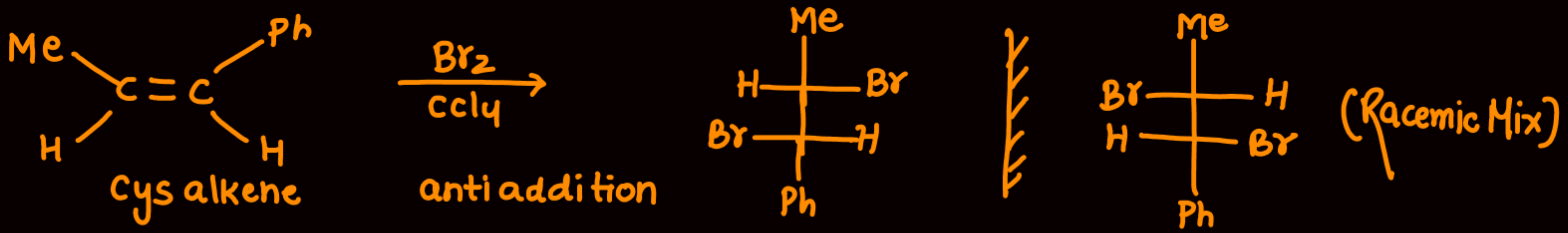
Important

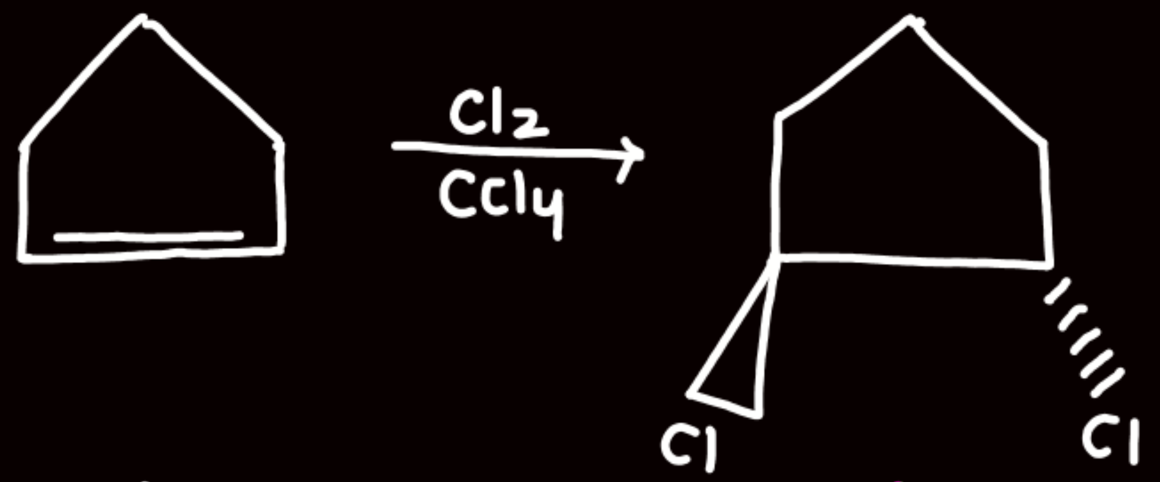
- anti
- C A R (cys) → Racemic
- T A M (Trans) → Meso, anti

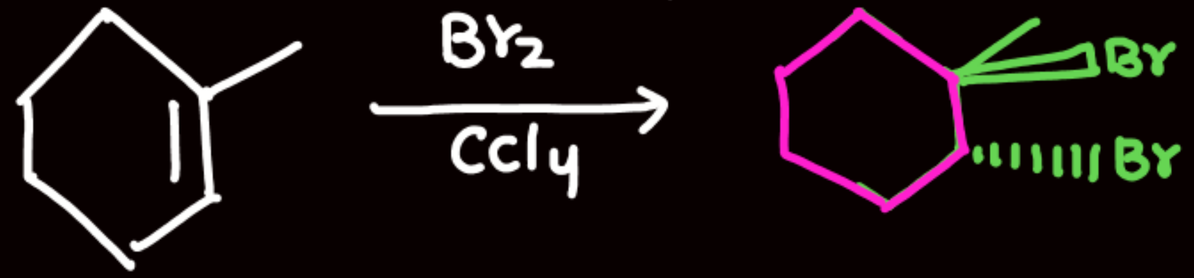


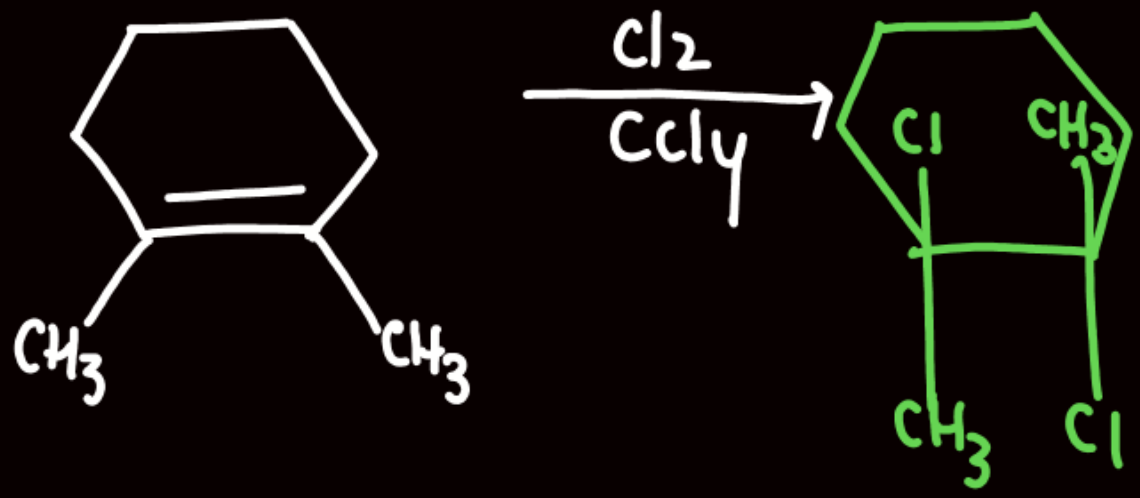




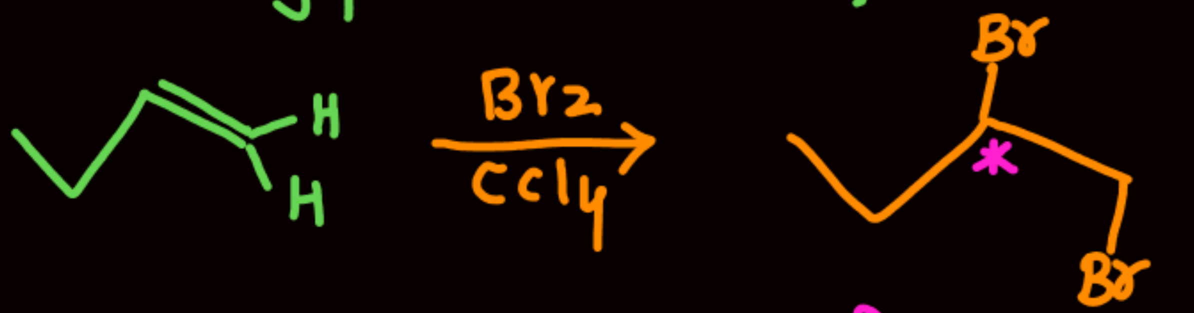








How many products will be formed —

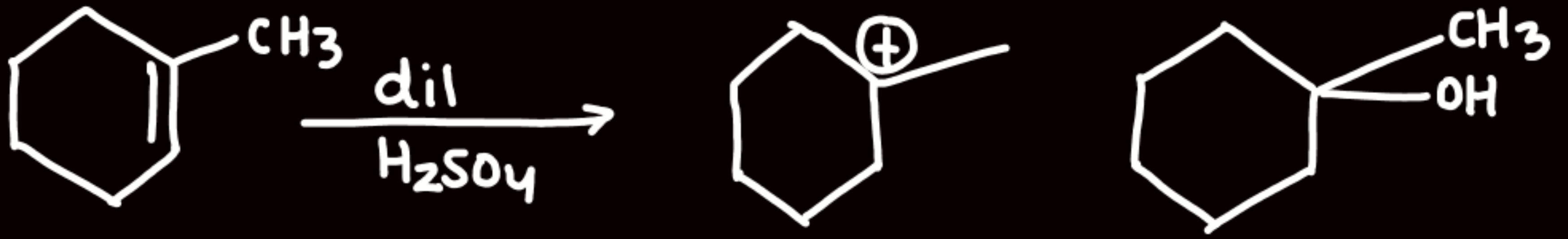


2 product

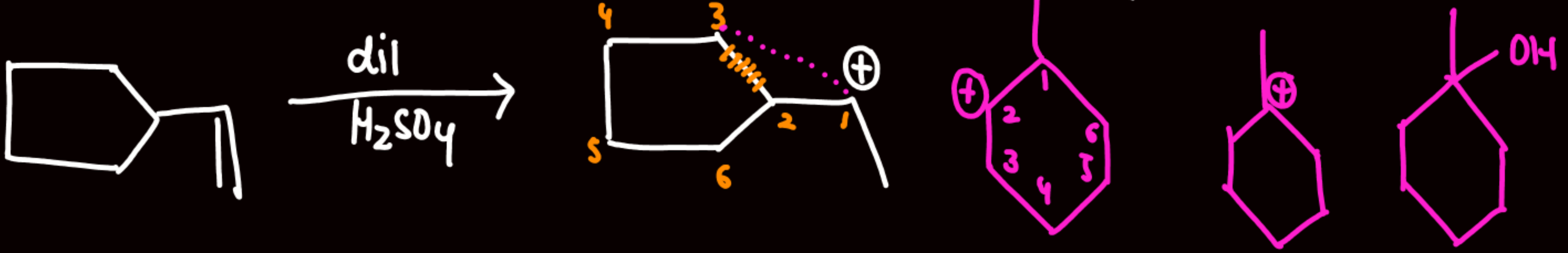
Addition of H_2O

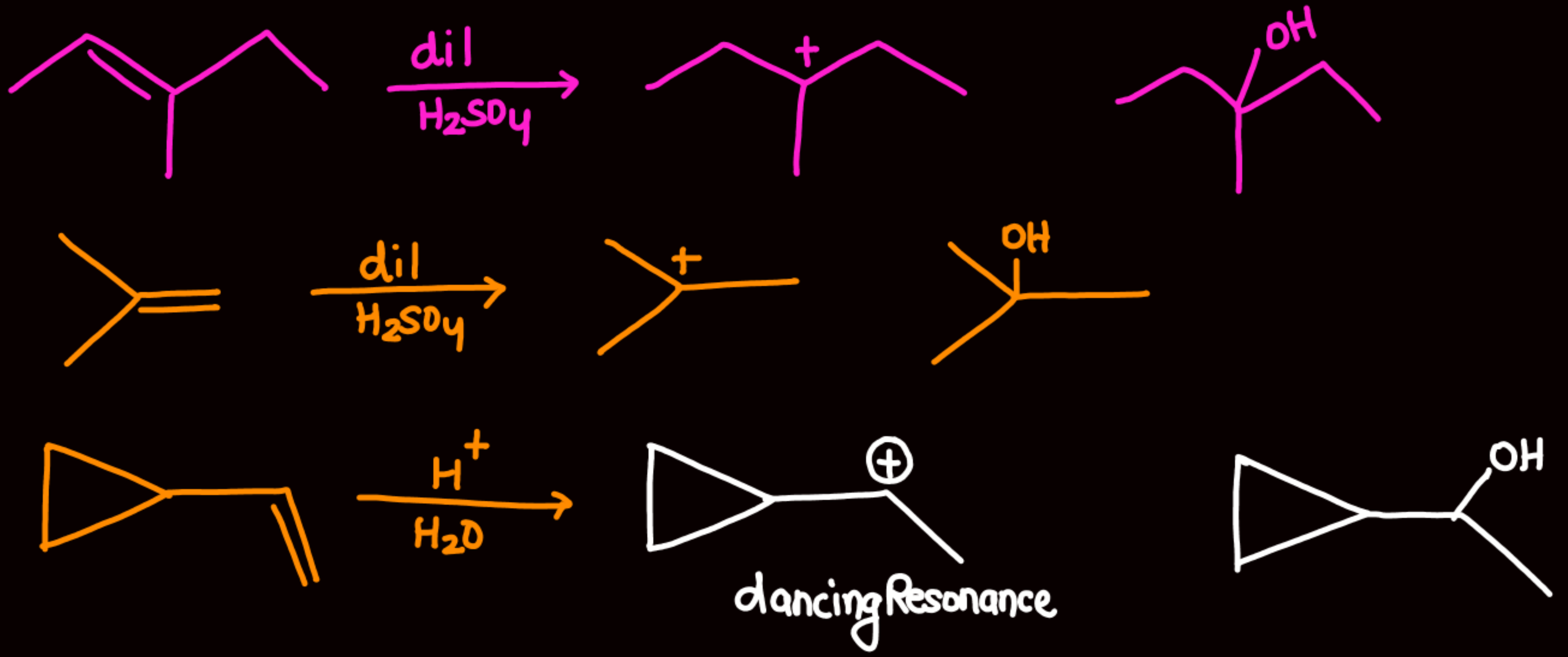
· Carbocation Form → Rearrange → OH^- attack ·











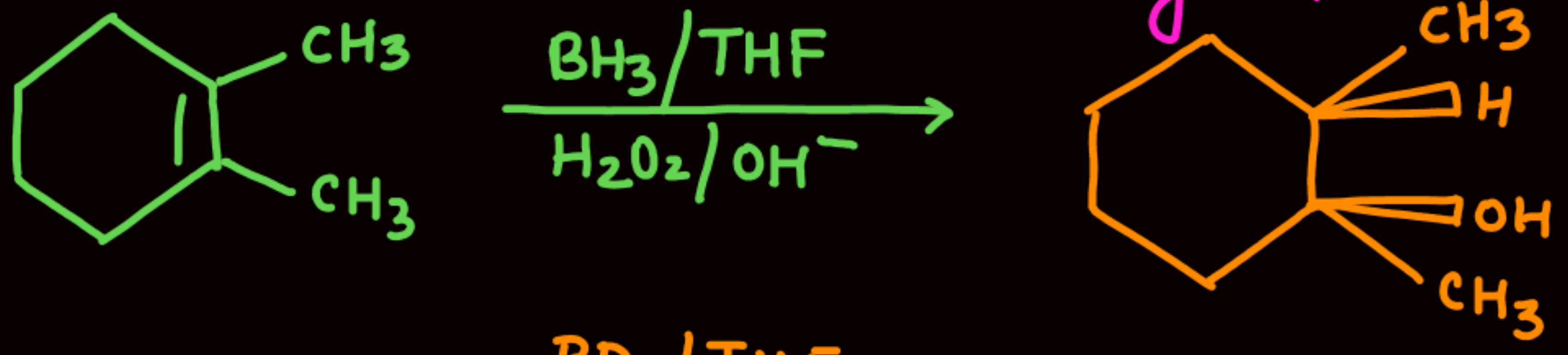
$$Ph-CH=CH-CH_3 \xrightarrow[H_2SO_4]{dil} Ph-\overset{\oplus}{C}H-CH_2-CH_3 \xrightarrow{OH^-} Ph-\underset{OH}{CH}-CH_2-CH_3$$

HydroBoration-oxidation (HBO) → H_2O addition

- addition of H_2O with antimarkovnikov Rule
- $\xrightarrow[H_2O_2/OH^-]{BH_3/THF}$ (THF → TetraHydroFuran) or $\xrightarrow[H_2O_2/OH^-]{B_2H_6}$

H & OH का addition (H from BH_3; OH from H_2O_2/OH^-)

- No Carbocation Formation & No Rearrangement.



$$CH_3-CH=CH_2 \xrightarrow[H_2O_2/OH^-]{BD_3/THF} CH_3-CH(D)-CH_2(OH)$$

$$CH_3-CH=CH_2 \xrightarrow[D_2O_2/OD^-]{BD_3/THF} CH_3-CH(D)-CH_2(OD)$$

$$CH_3-CH=CH_2 \xrightarrow[D_2O_2/OD^-]{BH_3/THF} CH_3-CH(H)-CH_2(OD)$$

Oxymercuration-Demercuration (OMDM)

- addition of H_2O with Markovnikov Rule.
- $\xrightarrow[NaBH_4]{Hg(OAc)_2/THF/H_2O}$
- no Carbocation formation & no rearrangement.

H_2O	$NaBH_4$
↓	↓
OH	H

$$CH_3-CH=CH_2 \xrightarrow[NaBH_4]{Hg(OAc)_2/H_2O} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle H}{\overset{|}{CH_2}}$$

$$\xrightarrow[NaBH_4]{Hg(OAc)_2/D_2O} CH_3-\underset{\displaystyle OD}{\underset{|}{CH}}-\overset{\displaystyle H}{\overset{|}{CH_2}}$$

$$\xrightarrow[NaBD_4]{Hg(OAc)_2/D_2O} CH_3-\underset{\displaystyle OD}{\underset{|}{CH}}-\overset{\displaystyle D}{\overset{|}{CH_2}}$$

$$\xrightarrow[NaBD_4]{Hg(OAc)_2/H_2O} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle D}{\overset{|}{CH_2}}$$

Oxidation of Alkene

(i) Combustion (PPCH)

$$C_nH_{2n} + \left(\frac{3n}{2}\right) O_2 \longrightarrow n\,CO_2 + n\,H_2O$$

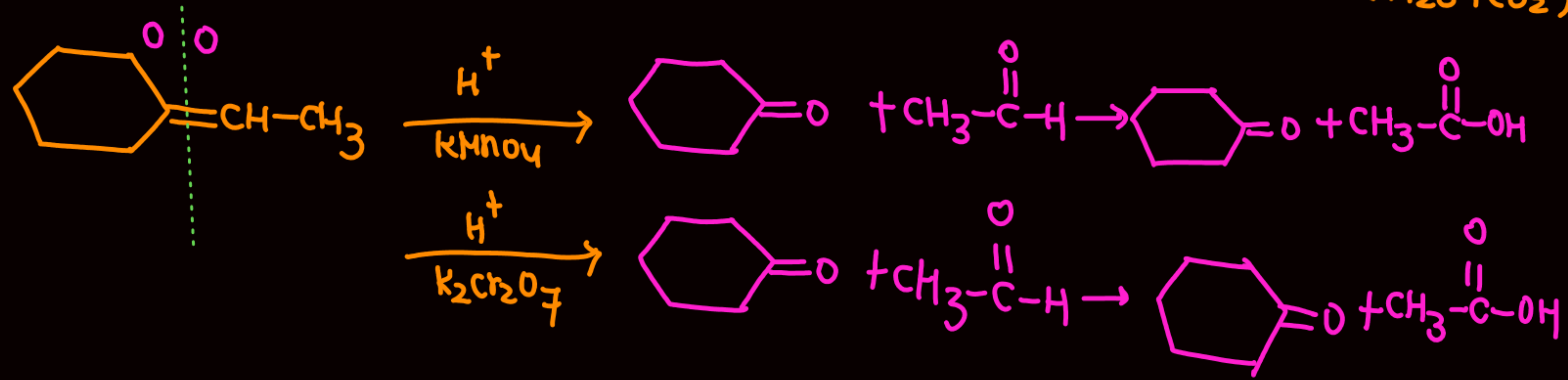
$$C_4H_8 + 6\,O_2 \longrightarrow 4\,CO_2 + 4\,H_2O$$

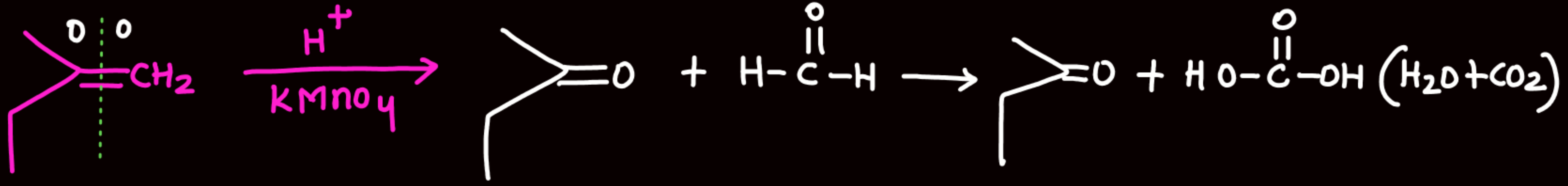
(ii) Oxidation with Strong oxidising agent ($KMnO_4$, $K_2Cr_2O_7$)

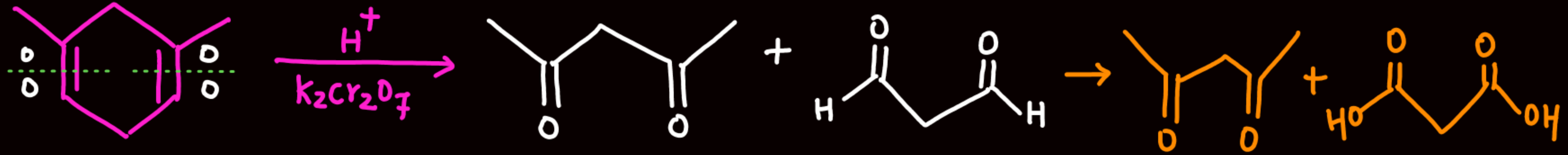
Q1 $CH_3-CH=CH_2 \xrightarrow[KMnO_4]{H^+} CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-OH$ ($H_2O + CO_2$)

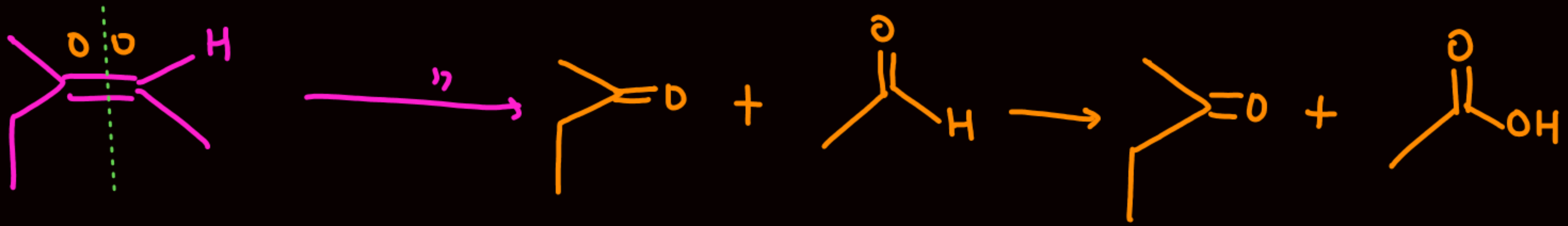
$\xrightarrow[K_2Cr_2O_7]{H^+} CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-OH$ ($H_2O + CO_2$)

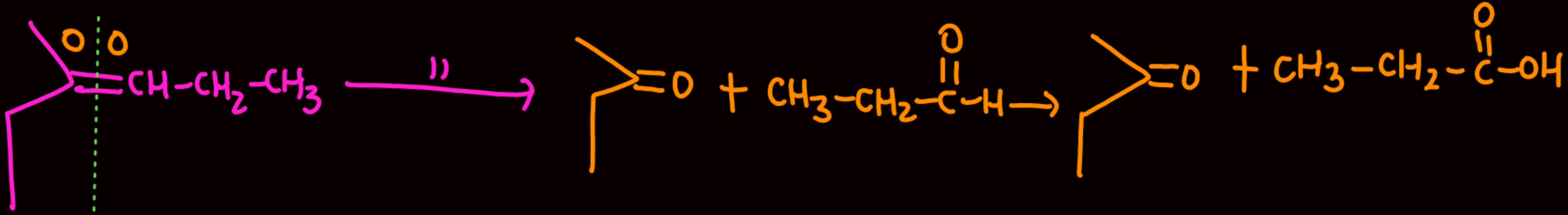
Q2




CH2
H+
KMnO4
H–C–H
HO–C–OH (H2O+CO2)


H+
K2Cr2O7
HO
OH


H
OH


CH–CH2–CH3
CH3–CH2–C–H
CH3–CH2–C–OH

Comeback

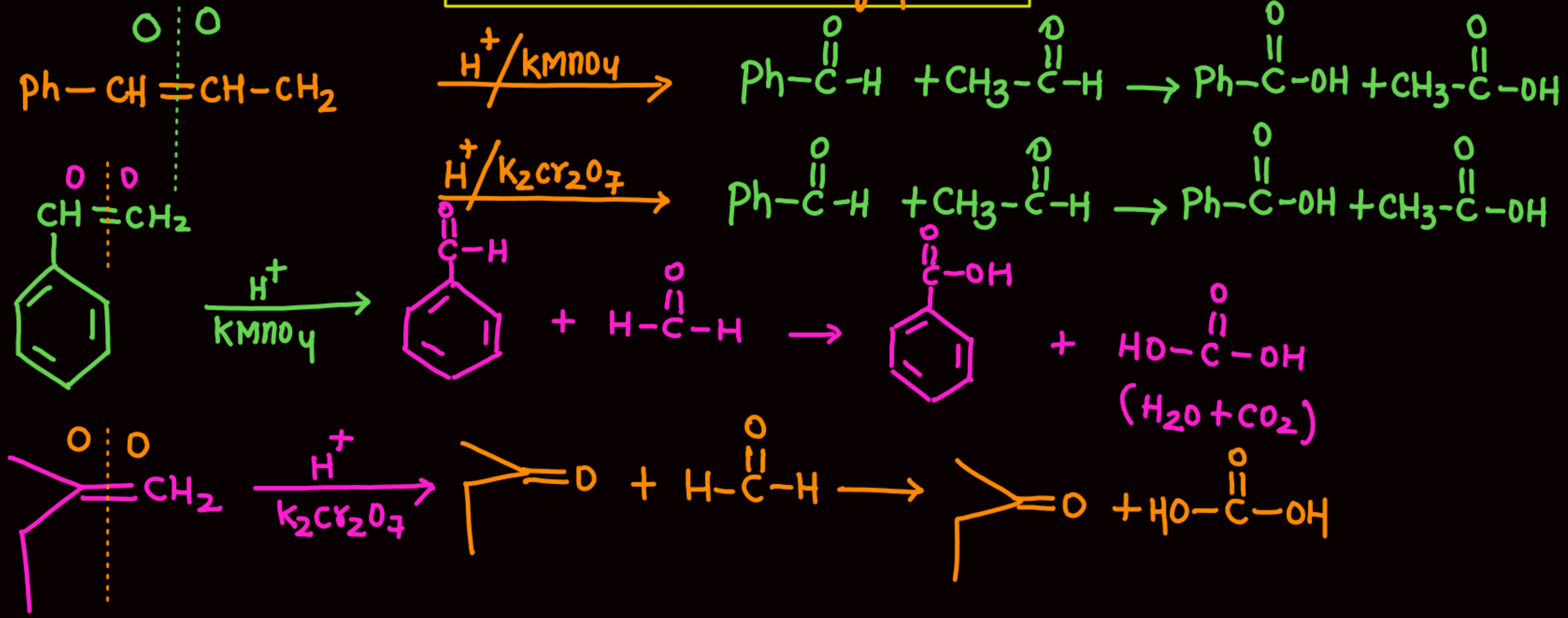
t.me/VTSIR1

Chapter list (84)

14chap → oneshot

70

Oxidation Reaction of Alkene



Addition of Cold $KMnO_4$ (Bayer's Reagent)

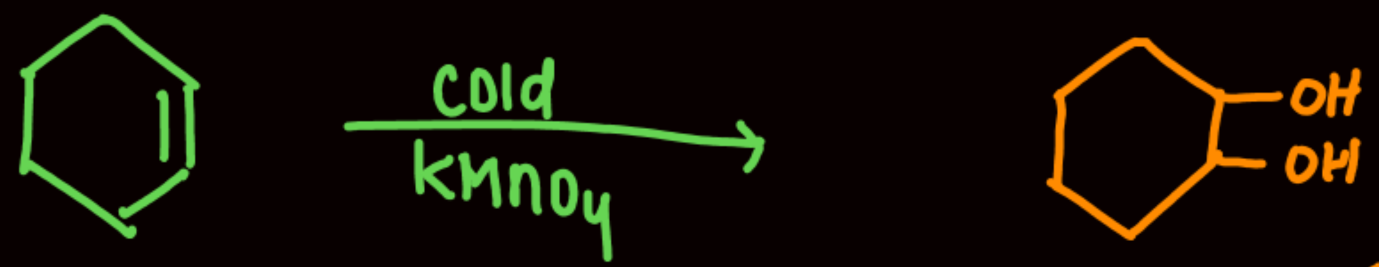
Bayer's Reagent → Cold $KMnO_4$ / alkaline $KMnO_4$ / dil $KMnO_4$
↳ Color (Magenta Pink)

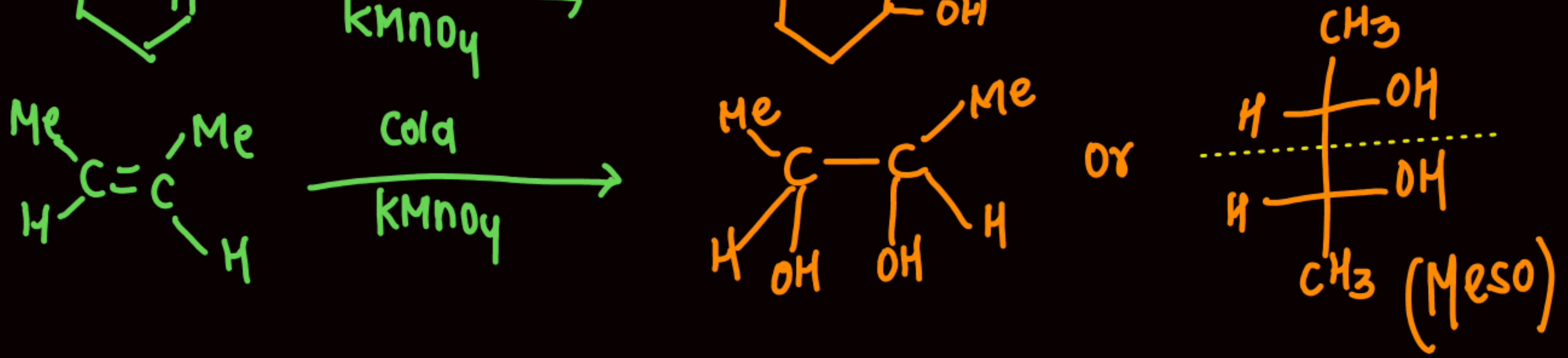
$$CH_3-CH=CH_2 \xrightarrow{\text{alkaline } KMnO_4} CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}$$

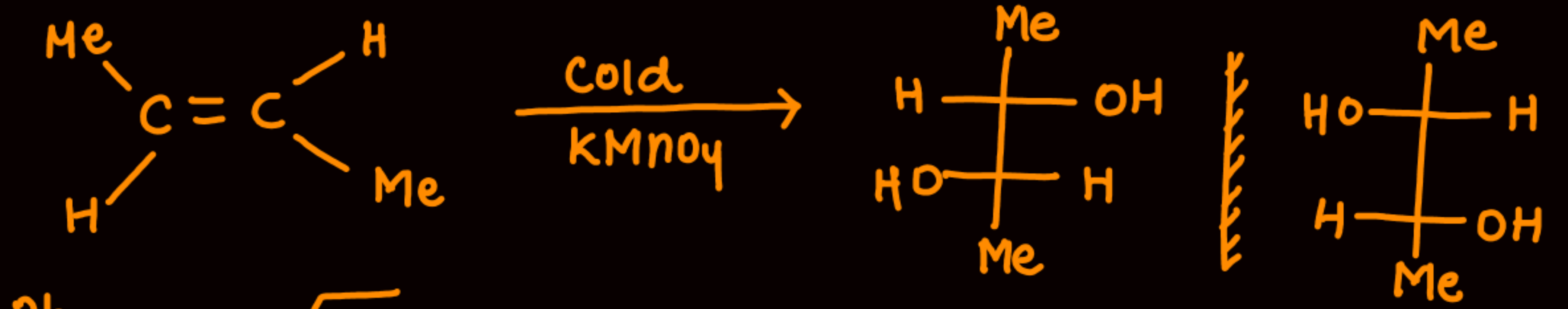
vicinal diol (Syn addition)

- Used for Test of Unsaturation.
- Syn addition of OH on both carbon of alkene.
- Bayer's Reagent becomes Colorless from magenta Pink after reaction.

$$CH_2=CH_2 \xrightarrow[KMnO_4]{Cold} \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}}$$



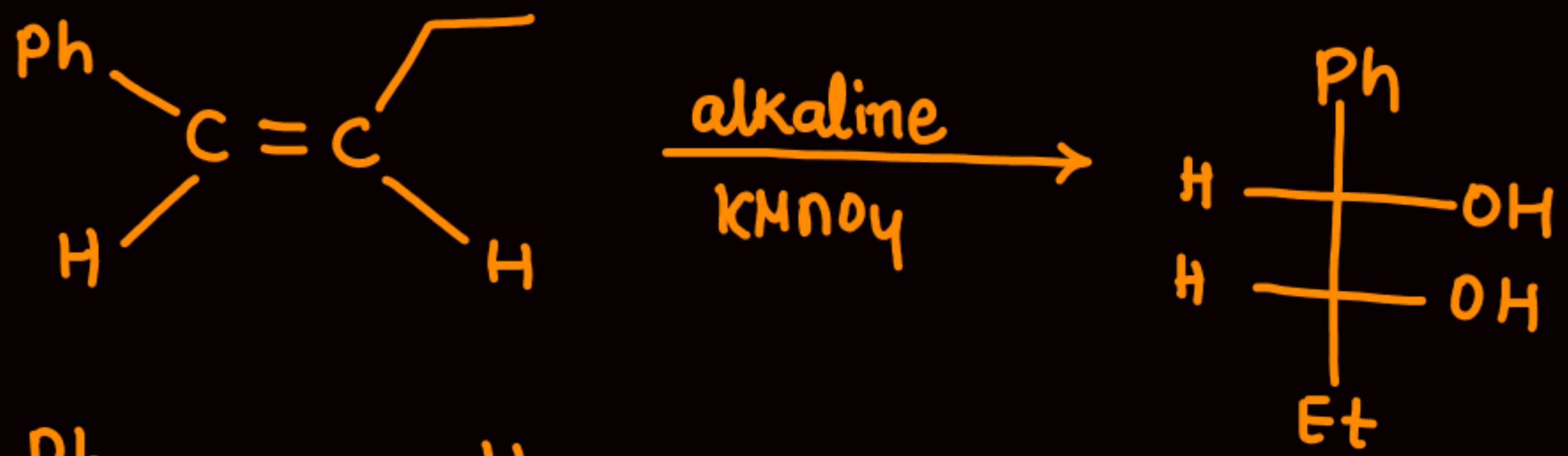


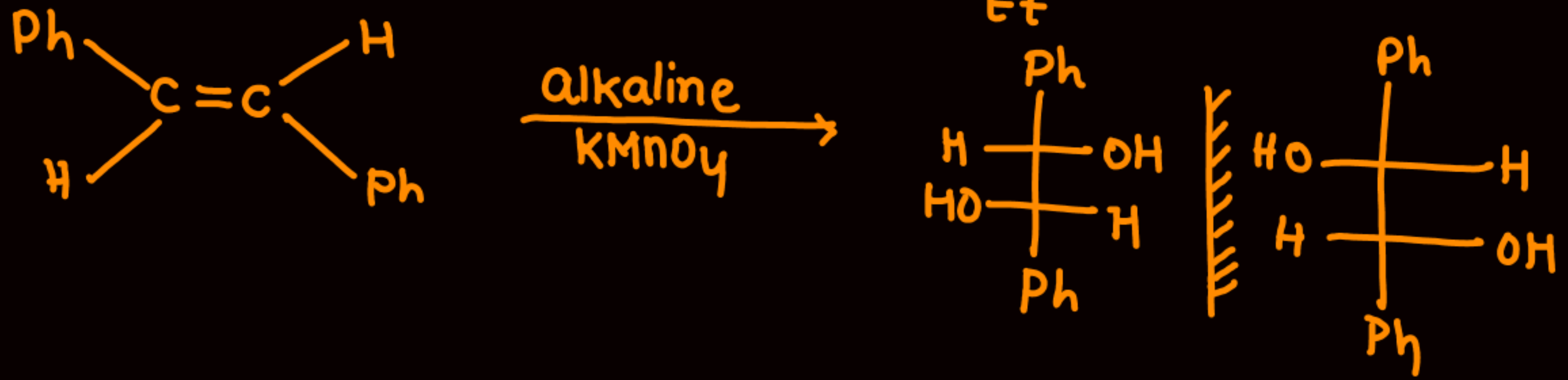


Racemic mix

CSE — Erythro

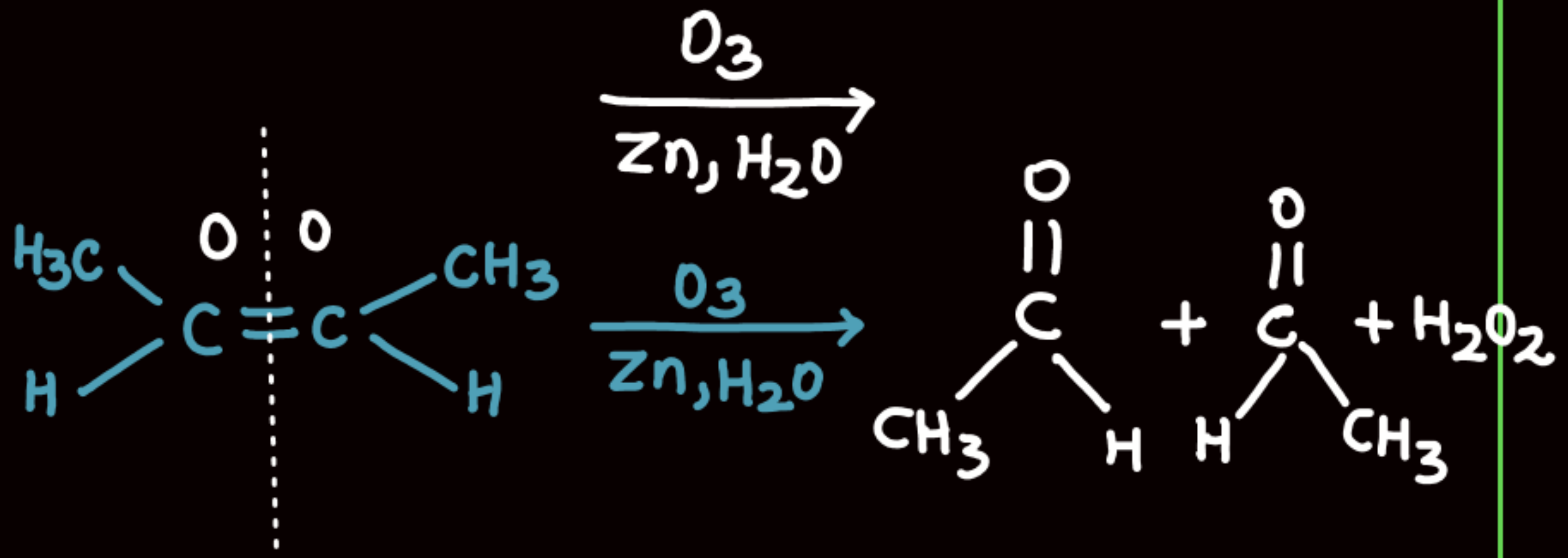
TST — Threo





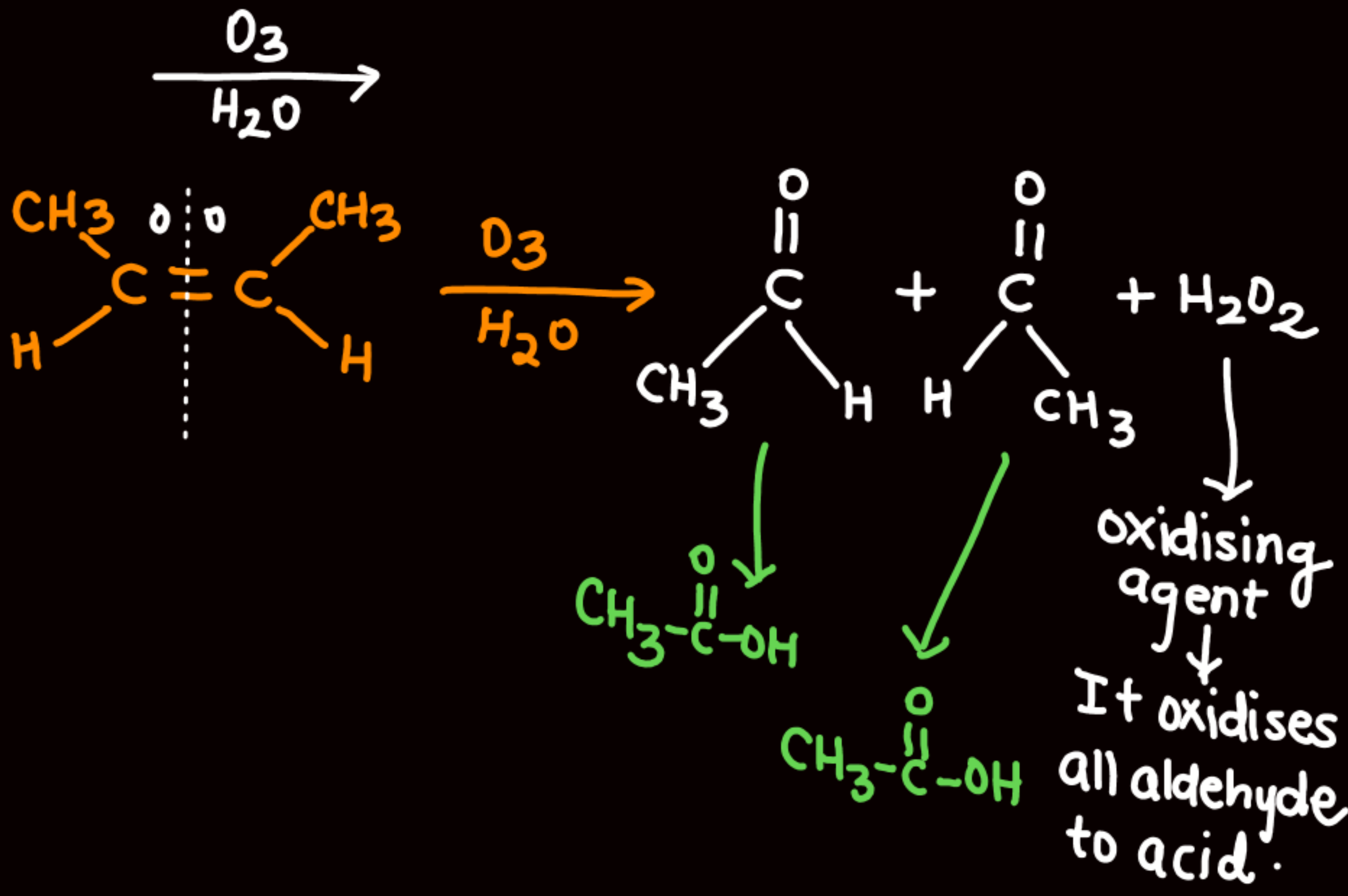
Ozonolysis

Reductive ozonolysis

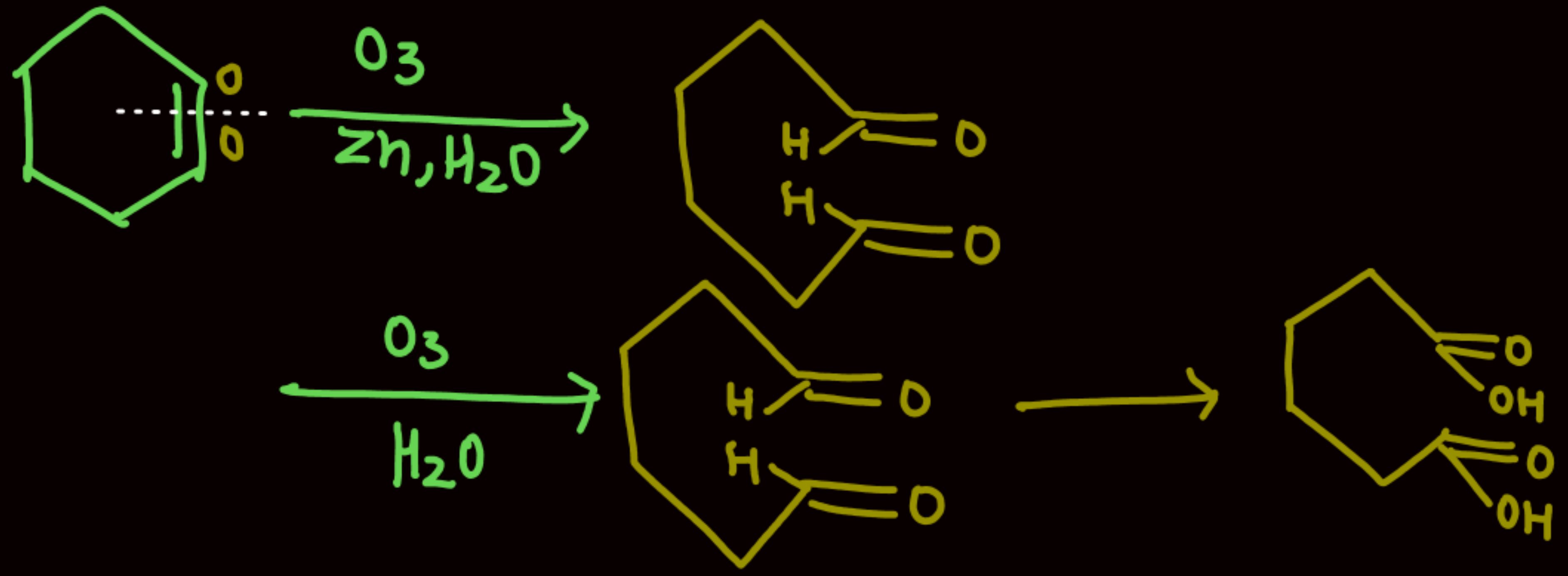


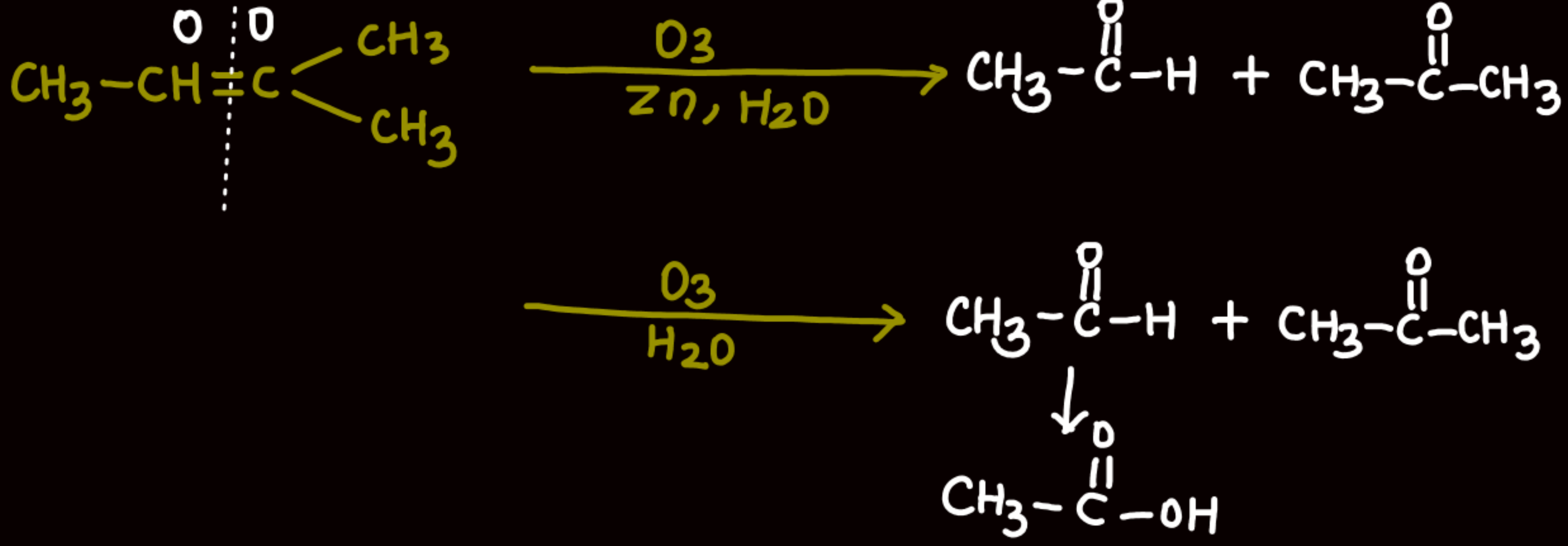
$Zn + H_2O_2 \longrightarrow ZnO + H_2O$

Oxidative ozonolysis



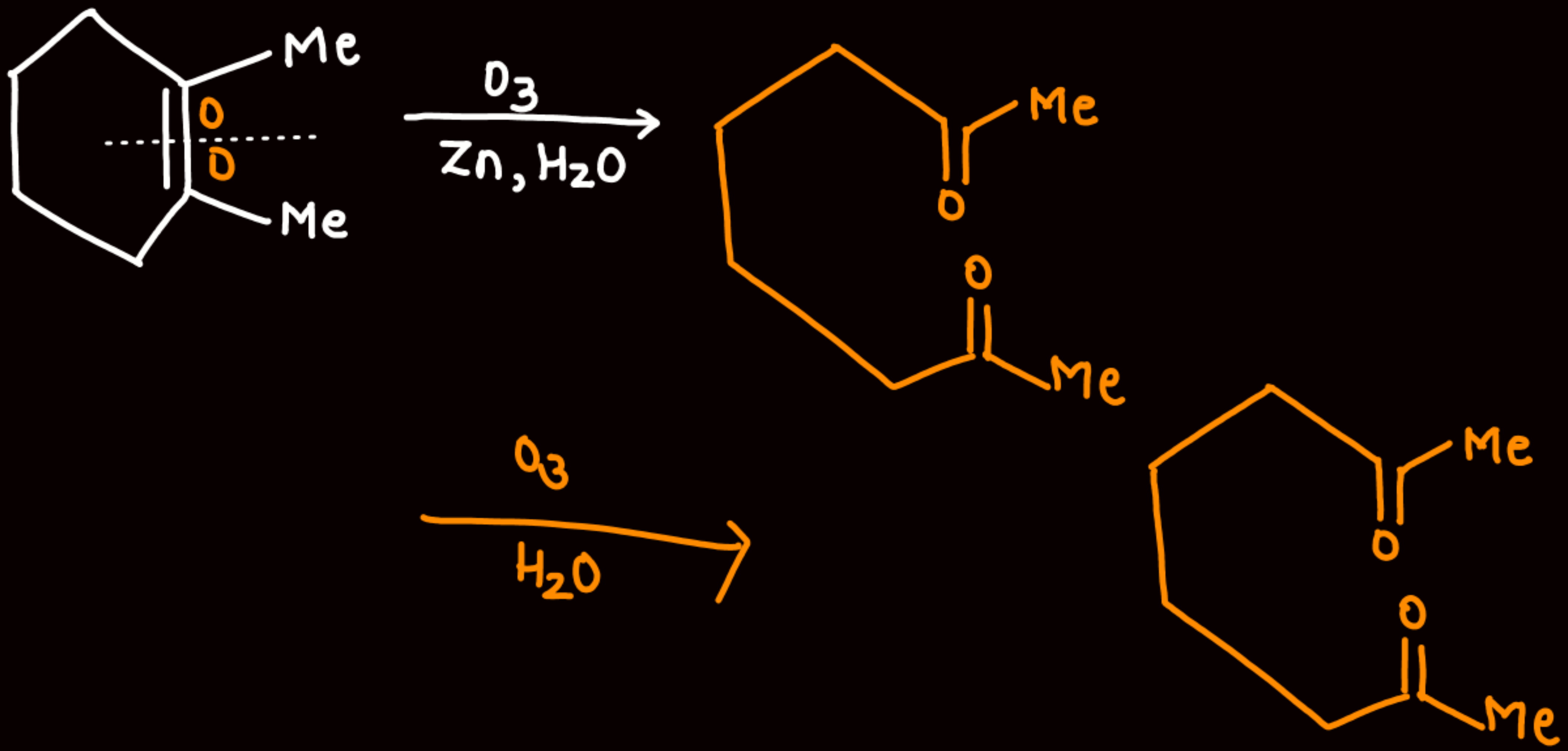
Que



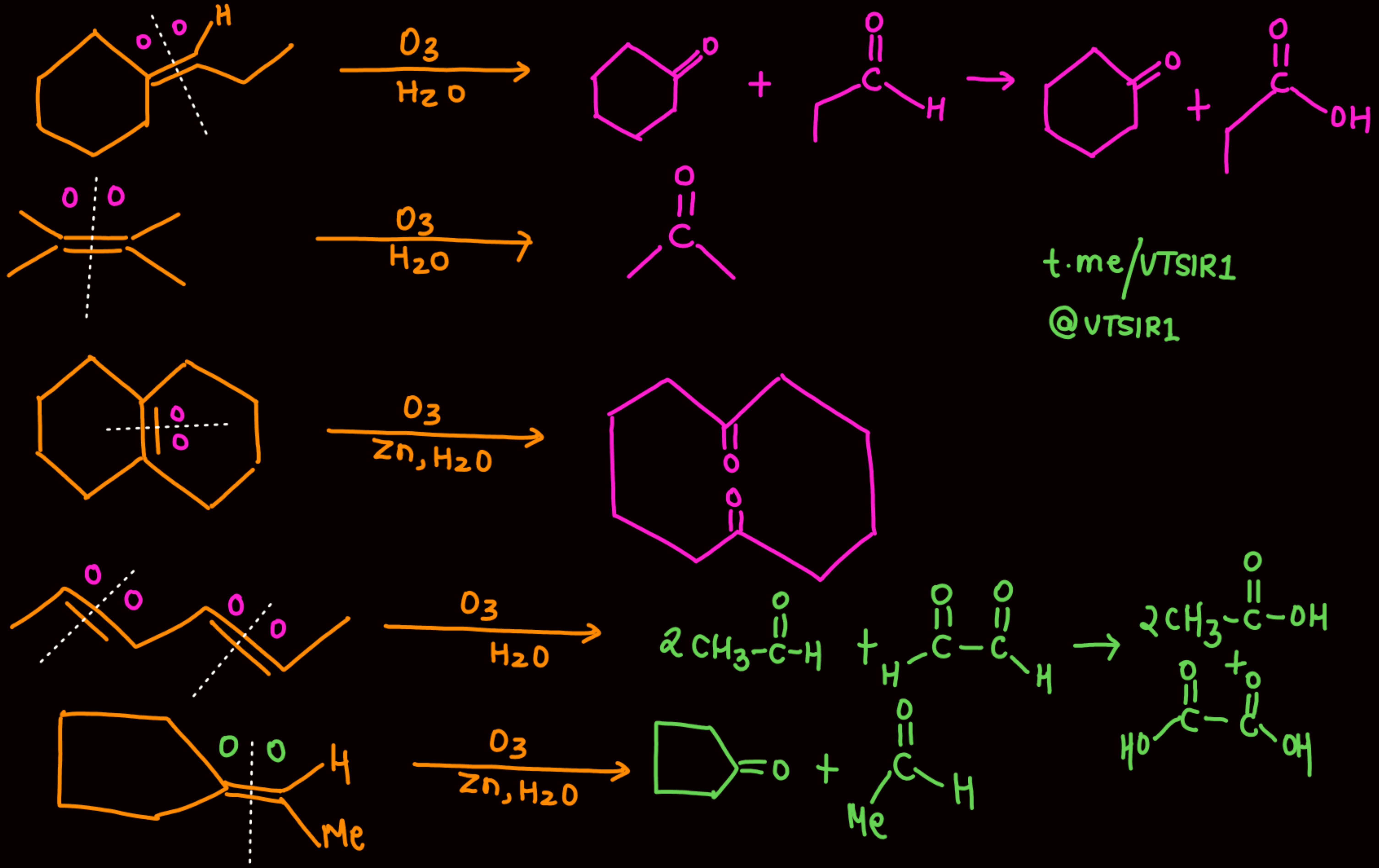


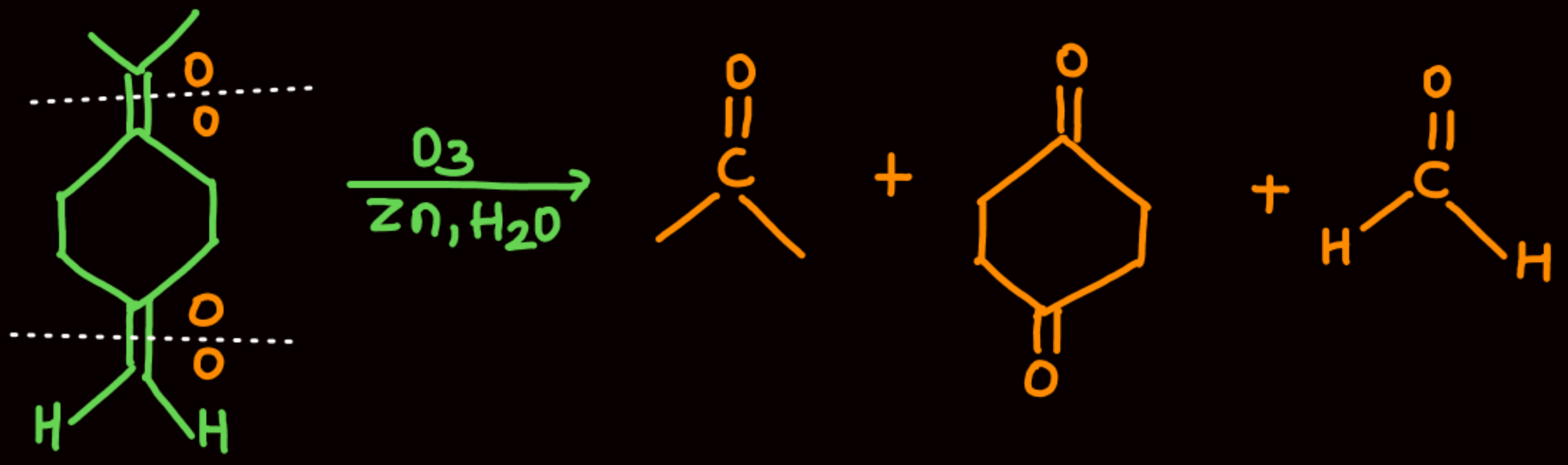
O O
CH3–CH=C(CH3)CH3
O3
Zn, H2O
CH3–C(=O)–H + CH3–C(=O)–CH3
O3
H2O
CH3–C(=O)–H + CH3–C(=O)–CH3
CH3–C(=O)–OH

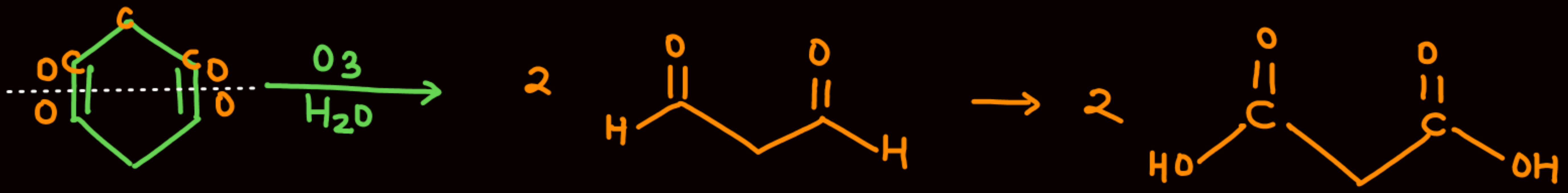
Q

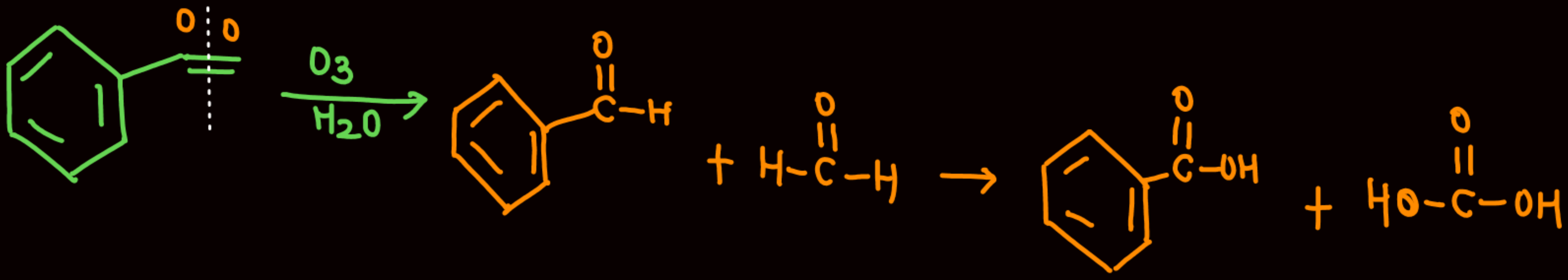


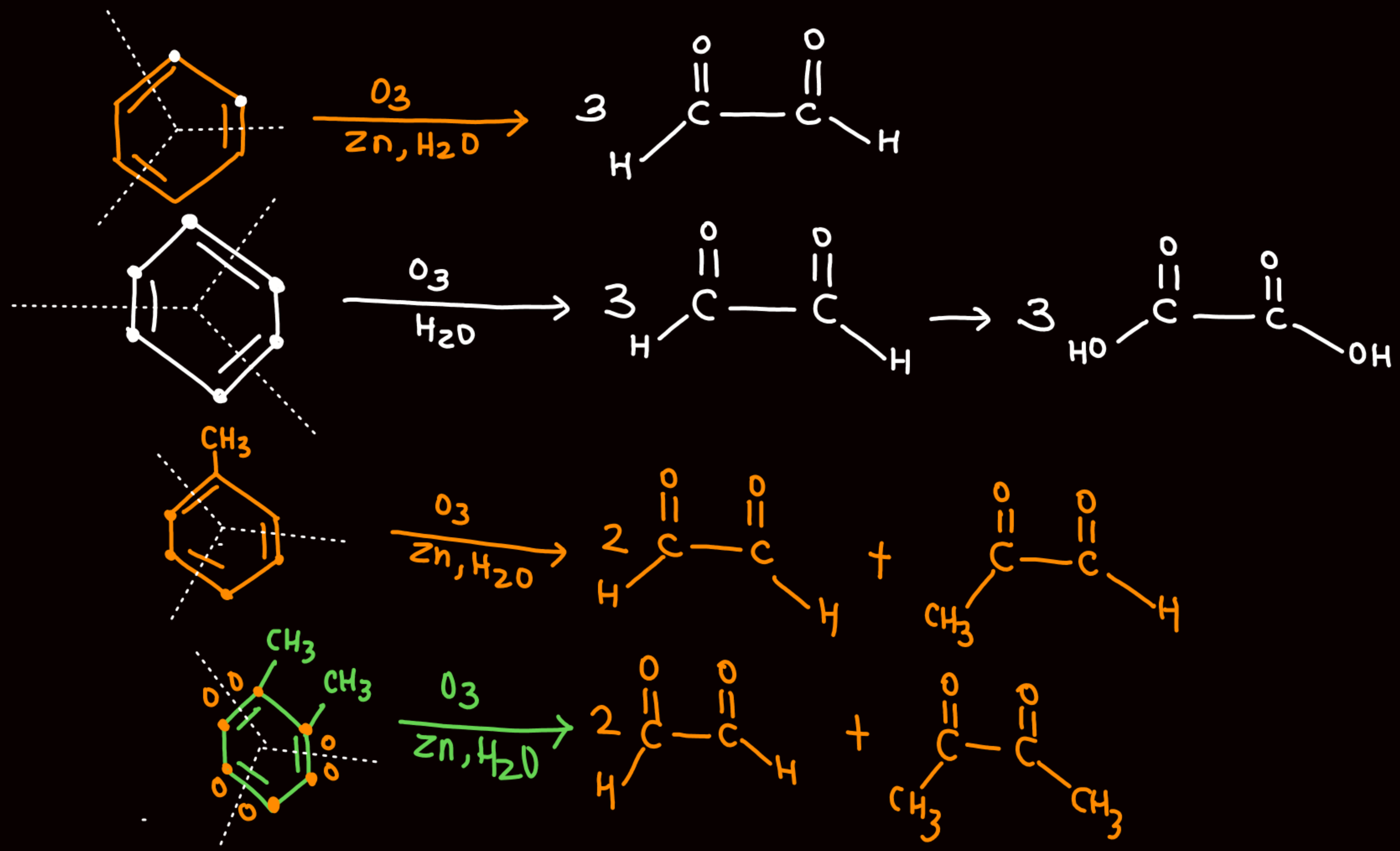
Me
Me
O
O
O3
Zn, H2O
Me
O
O
Me
O3
H2O
Me
O
O
Me


O O H
O_3
H_2O
O
O O
+
OH
O O
O_3
H_2O
O
C
O
O
O_3
Zn, H_2O
O
O
O O O O
O_3
H_2O
2 CH_3-C-H
O
+ H-C-C-H
O O
2 CH_3-C-OH
+
HO-C-C-OH
O O O O H Me
O_3
Zn, H_2O
=O
+
Me-C-H
O

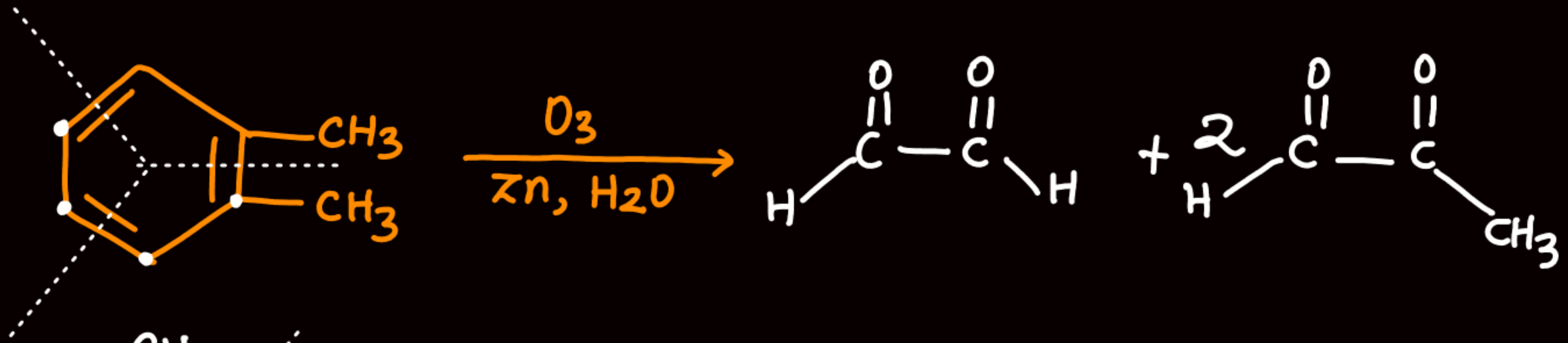

O3
Zn, H2O

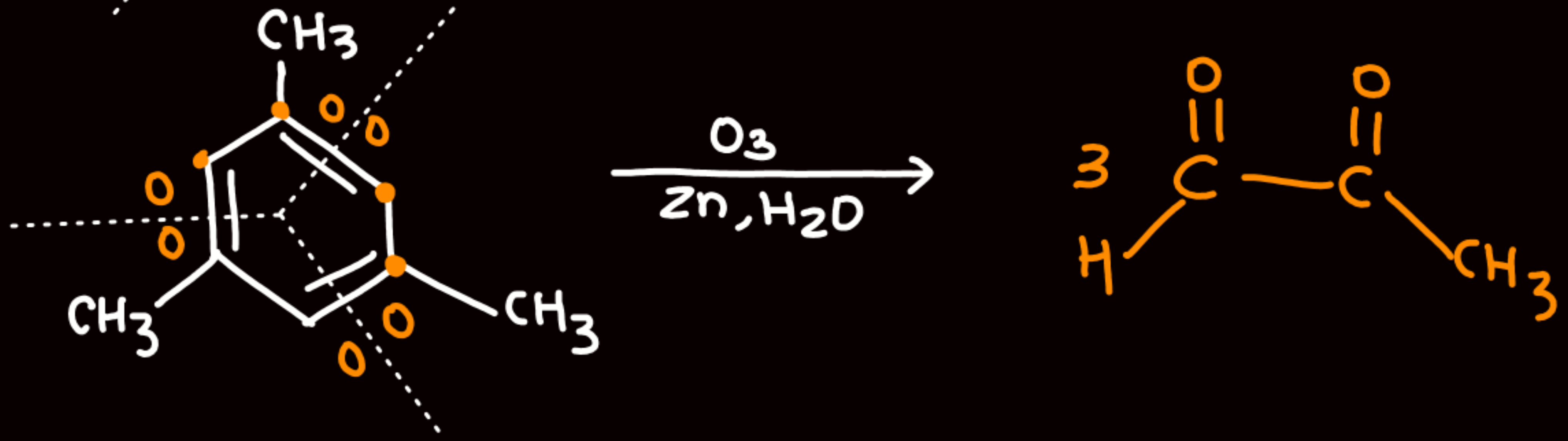

O3
H2O

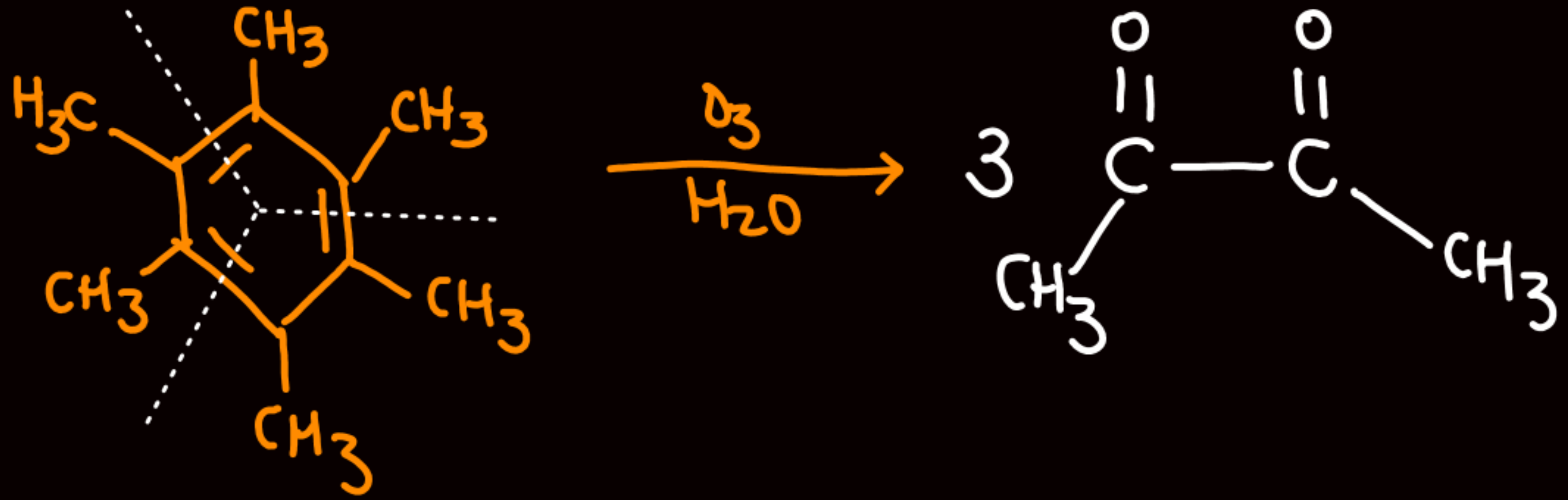

O3
H2O



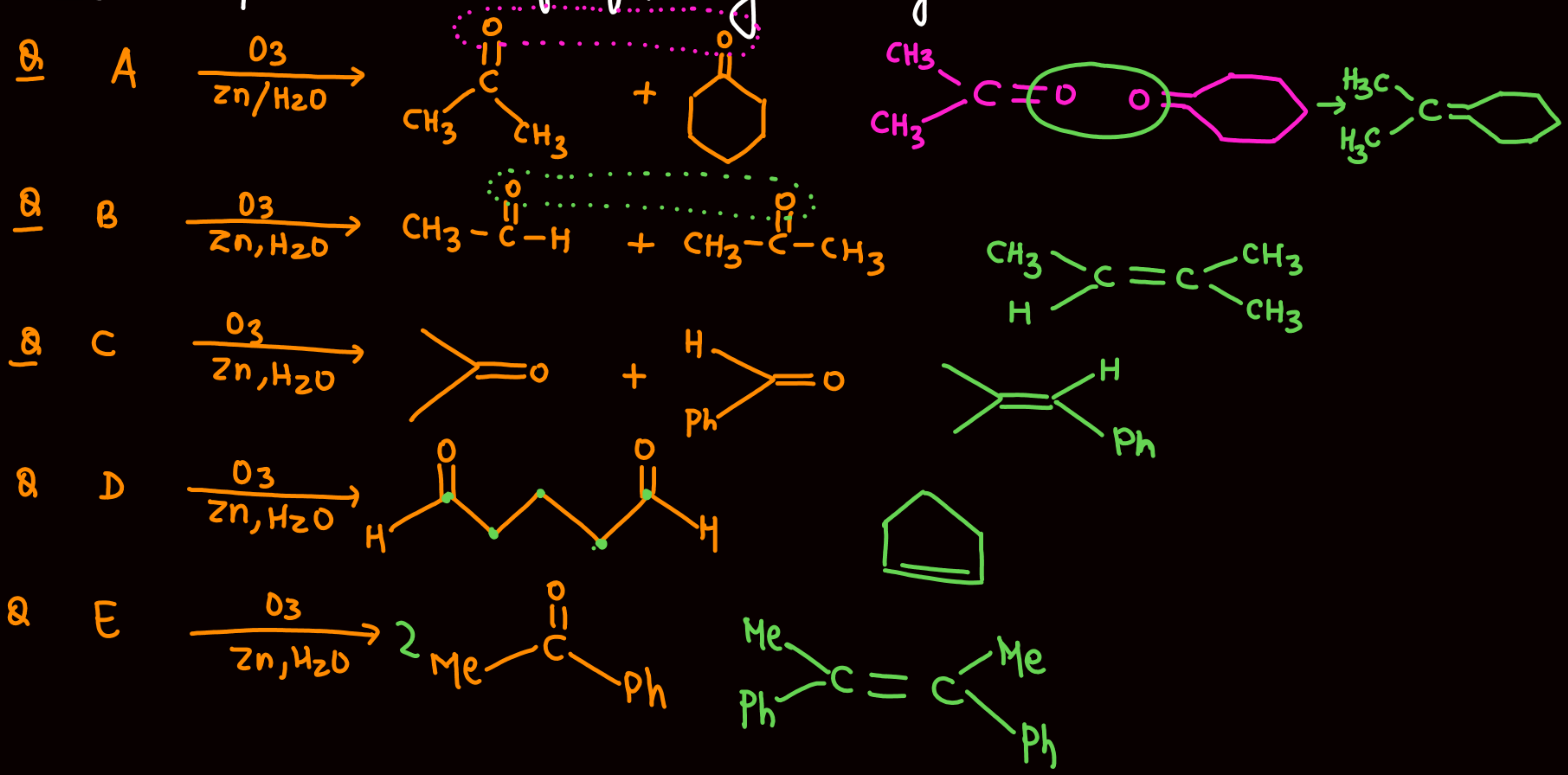
O3
Zn, H2O
3
O3
H2O
3
3
HO
OH
CH3
O3
Zn, H2O
2
+
CH3
CH3
CH3
O3
Zn, H2O
2
+
CH3
CH3


CH3
CH3
O3
Zn, H2O
O
C
H
+ 2
CH3


CH3
CH3
CH3
O3
Zn, H2O
3
O
C
H
CH3


CH3
H3C
CH3
CH3
CH3
CH3
O3
H2O
3
O
C
CH3

Que write possible alkenes for following Ozonolysis reaction –

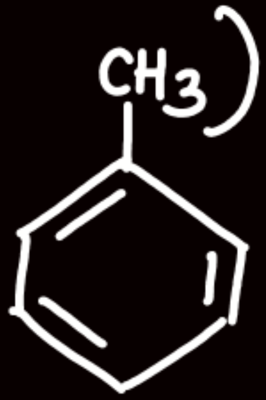


Substitution Reaction

→ allylic & Benzylic Substitution

$CH_2=CH-CH_3$

allylic position

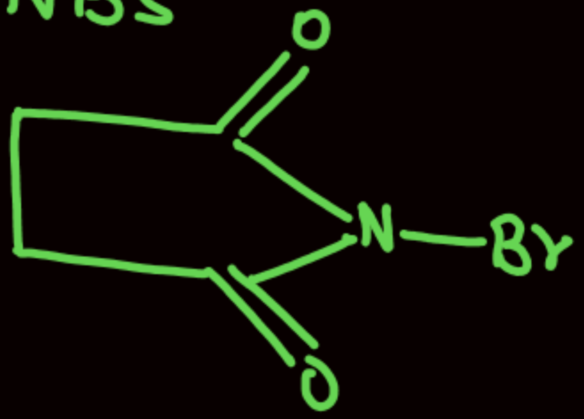


Benzylic position

allylic/Benzylic [Chlorine Substitution] $\xrightarrow[500^\circ C/773K]{Cl_2}$

allylic/Benzylic [Bromine Substitution] N-Bromo Succinamide

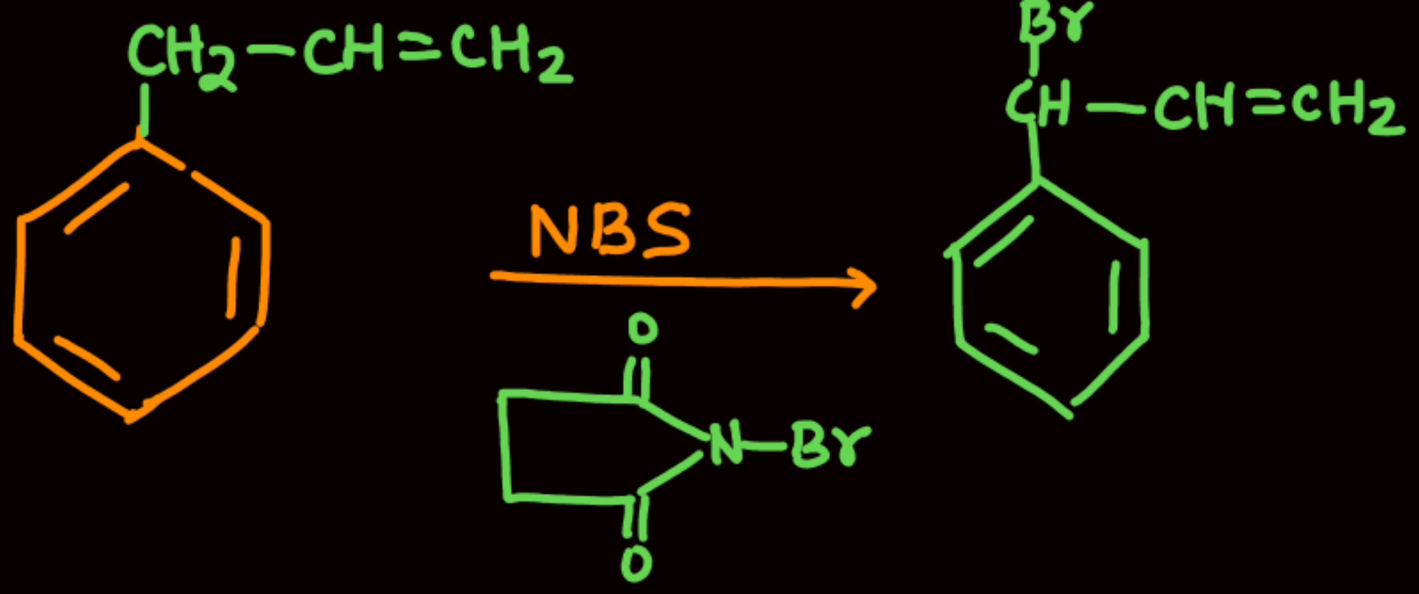
NBS



Q ① $CH_3-CH=CH_2 \xrightarrow[773K]{Cl_2} CH_2(Cl)-CH=CH_2$

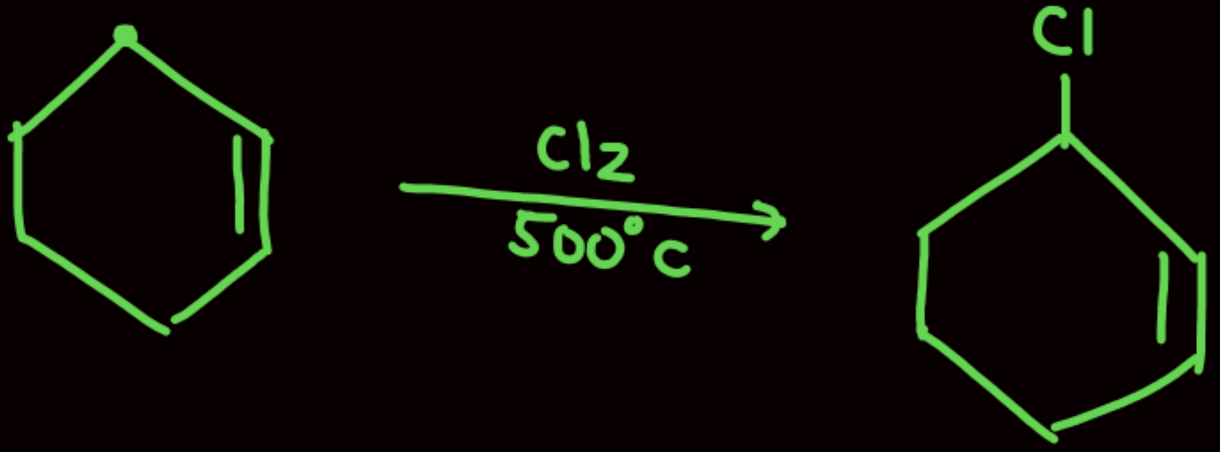
② $CH_3-CH=CH_2 \xrightarrow{NBS} CH_2(Br)-CH=CH_2$

3



$CH_2-CH=CH_2$
NBS
N–Br
O
O
Br
$CH-CH=CH_2$

4



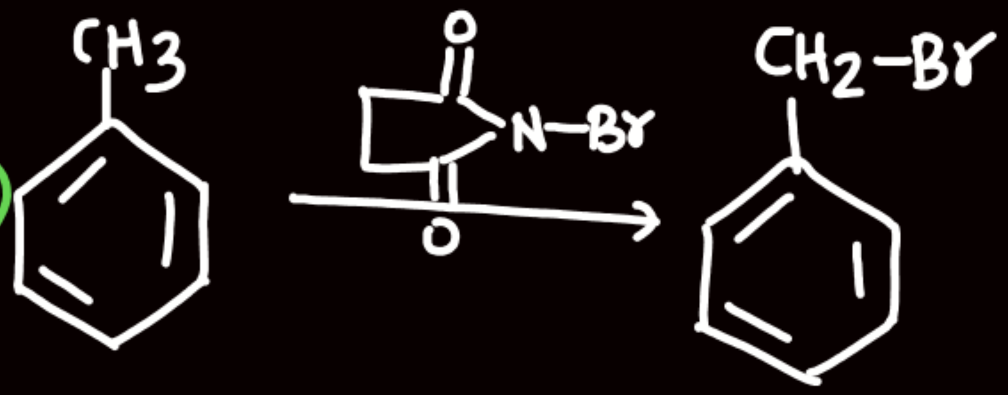
Cl_2
500°C
Cl

5



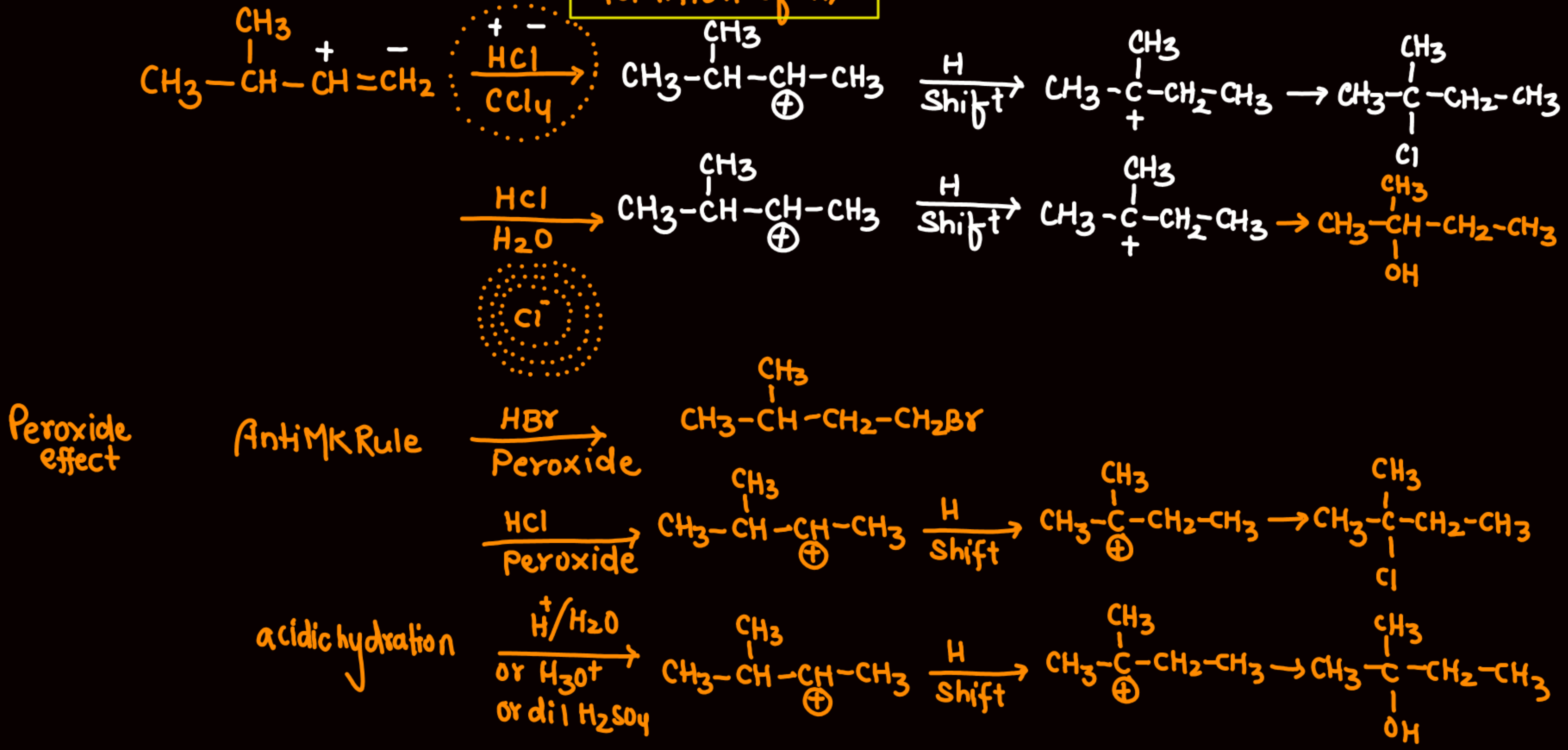
NBS
Br

6



CH_3
O
N–Br
O
CH_2-Br

Addition of HX



Addition of Conc. H_2SO_4

Conc H_2SO_4 → Electrophile ≡ H^+

nucleophile ≡ HSO_4^- / $^-O-SO_2-OH$ / $^-O-SO_3H$

$H-O-S(=O)_2-OH$

$$CH_3-\overset{+}{C}H=\overset{-}{C}H_2 \xrightarrow{\text{conc } H_2SO_4} CH_3-\overset{+}{C}H-CH_3 \longrightarrow CH_3-\underset{HSO_4}{CH}-CH_3 \;/\; CH_3-\underset{OSO_2OH}{CH}-CH_3 \;/\; CH_3-\underset{OSO_3H}{CH}-CH_3$$

(POC) This reaction is used to <u>separate alkene from alkane</u>.

CH_3-CH_3 → ×

&

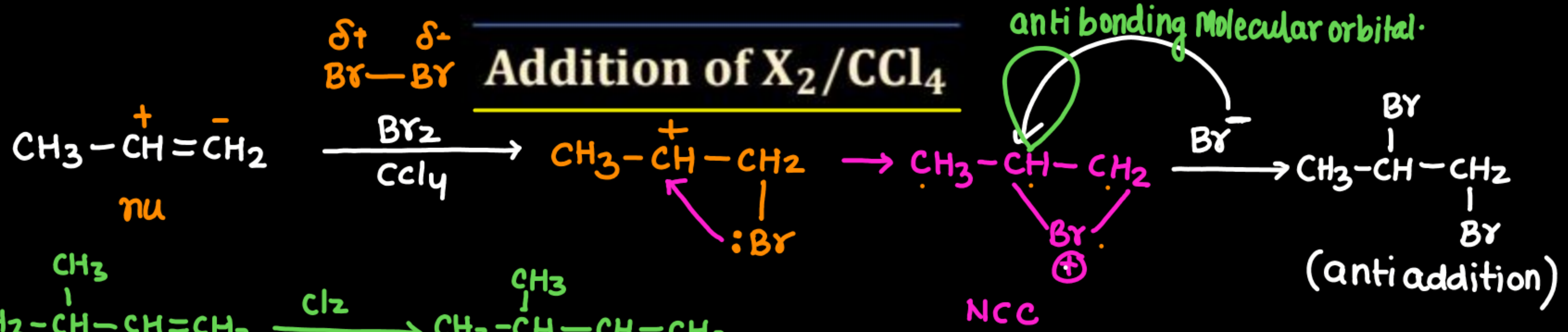
$CH_2=CH_2$ → ✓

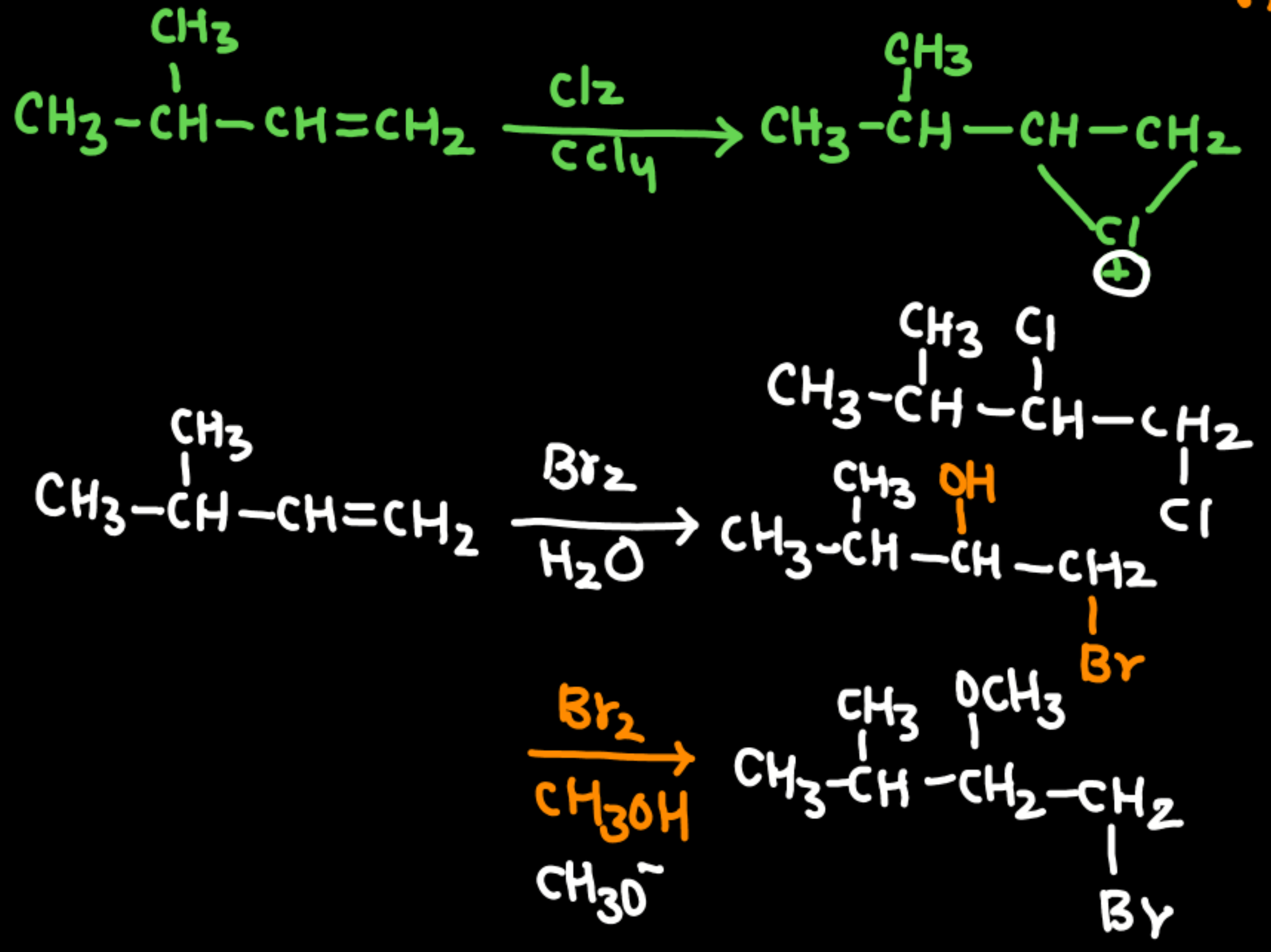
$$\xrightarrow{\text{Conc } H_2SO_4} \underset{H}{CH_2}-\underset{HSO_4}{CH_2}$$

Salt

alkyl Hydrogen Sulphate

Addition of X_2/CCl_4





- * Non classical carbocation.
- * Octet complete (no rearrangement).
- * cyclic halonium ion.
- * cyclic Bromonium ion.
- * 3member Ring (Repulsion) (unstable)

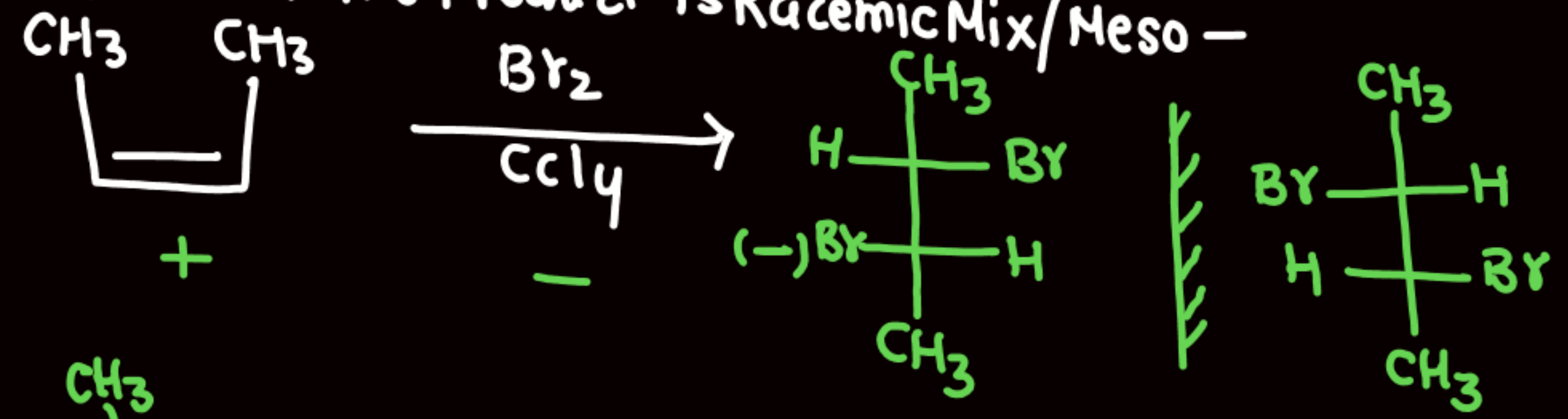
Same Side +
opp Side −

Stereochemistry of Reaction

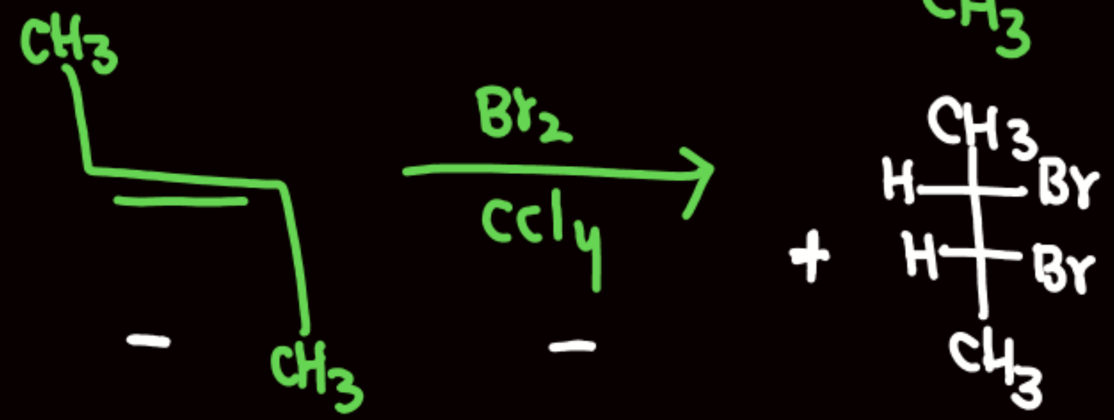
OT
SE

alkene	addition	Product		
cys +	syn +	+	Same Side	Erythro
cys +	anti −	−	opp Side	Threo
Trans −	syn +	−	opp Side	Threo
Trans −	anti −	+	Same Side	Erythro

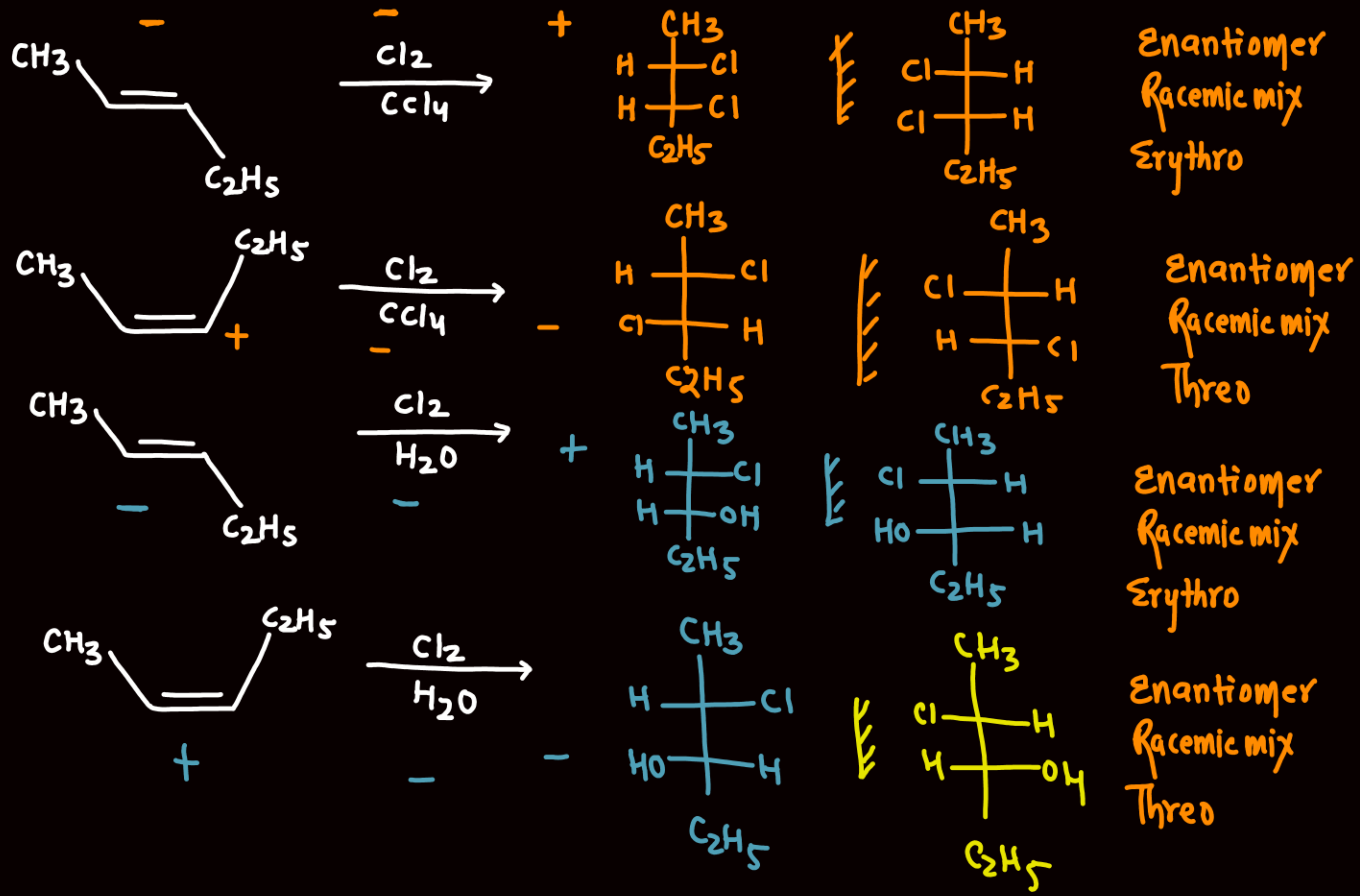
Que Find whether the Product is Racemic Mix/Meso −



Enantiomer
Racemic mix
Threo

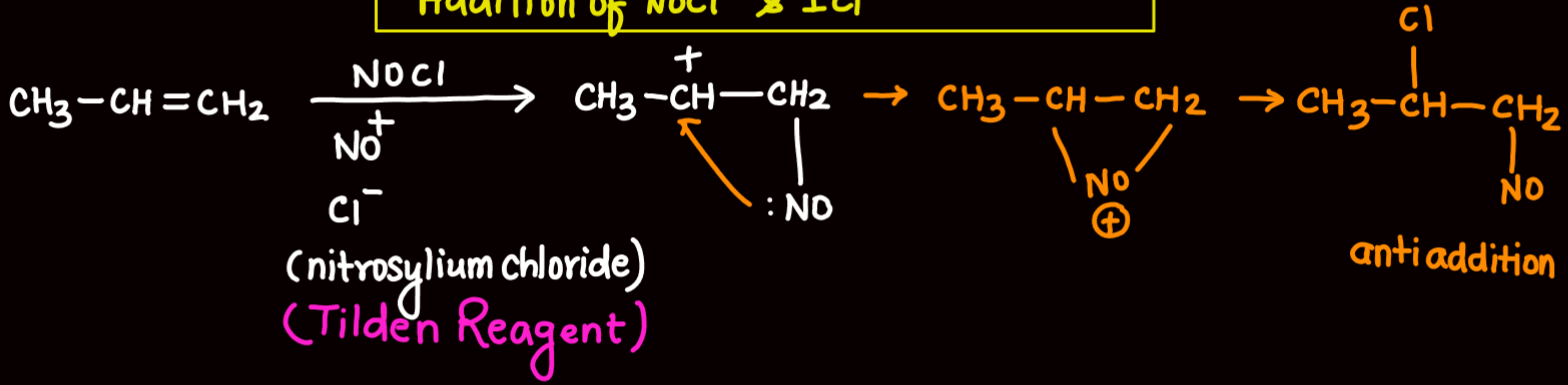


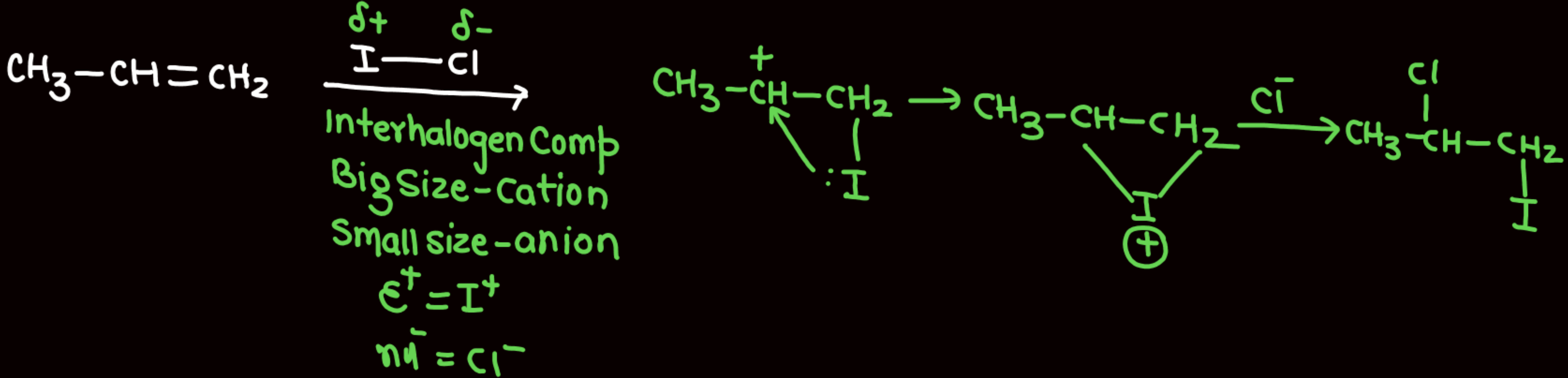
Meso
Erythro



CH3
C2H5
Cl2
CCl4
Enantiomer
Racemic mix
Erythro
Enantiomer
Racemic mix
Threo
Cl2
H2O
Enantiomer
Racemic mix
Erythro
Enantiomer
Racemic mix
Threo

Addition of NOCl & ICl





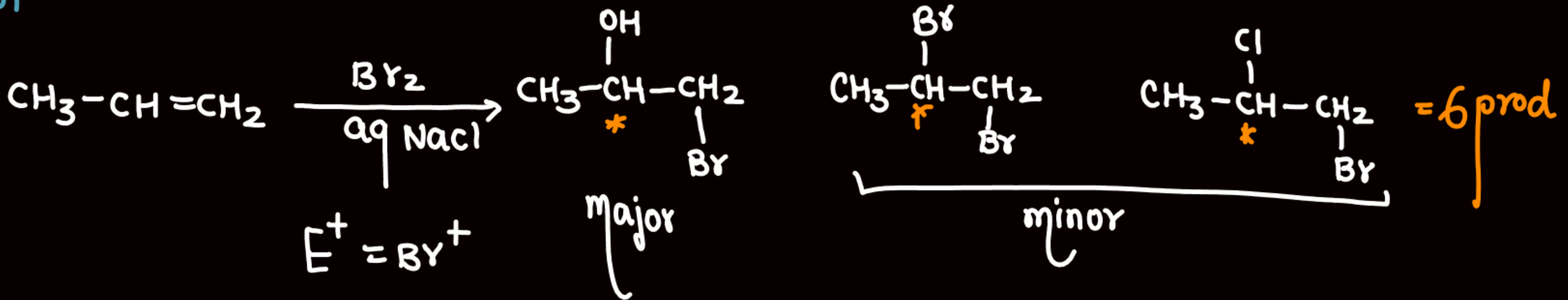
Que What is the product formed on reaction of Propene & Brine Solution —
aq NaCl

$CH_3-CH=CH_2$ (nu⁻) $\xrightarrow{\text{aq NaCl}}$ No reaction

- H_2O (Nu)
- Na^+ inert
- Cl^- (nu⁻)

(A) 1
(B) 2
(C) 3
~~(D)~~ NOT ✓

Que



$E^+ = Br^+$

$Nu^- = H_2O$
$= Cl^-$] minor
$= Br^-$]

ALKYNE

- Unsaturated Comp having atleast one Triple bond.
- DU = 2 · GF = C_nH_{2n-2}
- 1st member → C_2H_2 ethyne (acetylene)
-

$$\underset{1s}{H} - \underset{sp_x}{C} \equiv \underset{sp_x}{C} - \underset{1s}{H}$$

C–H = σ bond = 2 → sp–1s overlap
C–C = σ bond = 1 → sp–sp overlap
} Headon Overlap

C–C = π bond = 2 → 2p–2p Lateral overlap or Sideways overlap

Alkyne

Alkyne → Terminal / Non Terminal alkyne

Terminal

$CH_3-C\equiv CH$

↑ sp Carbon, High EN
↓
'H' is associated to more EN sp Carbon
↓
'H' → Acidic

Non Terminal alkyne

$CH_3-C\equiv C-CH_3$

↑ There is no acidic H

Preparation of Alkyne

① Industrial preparation of acetylene (C_2H_2)

① Calcium Carbide on reaction with H_2O

ALKYNE

Method of Preparation

1. From Carbide
2. alkyl halide
   - → Gem dihalide
   - → Vicinal dihalide
   - → Vicinal Tetrahalide
   - → Gem Trihalide
3. smaller alkyne ⟶ Higher alkyne
4. carboxylic acid ⟶ alkyne (PPCH)

Carbide → Alkyne

$\overset{+2}{Ca}\ \overset{-2}{C_2}$

① $CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

Calcium Carbide; C_2H_2 = ethyne (acetylene)

] Industrial preparation of ethyne (acetylene)

---

② $Be_2\overset{-4}{C} + H_2O \longrightarrow CH_4 + Be(OH)_2$

Berellium Carbide

③ $\overset{+12}{Al_4}\overset{-12}{C_3} + H_2O \longrightarrow CH_4 + Al(OH)_3$

Aluminium carbide

④ $Mg_2\overset{-4}{C_3} + H_2O \longrightarrow C_3H_4 + Mg(OH)_2$

Magnetium carbide; C_3H_4 = $CH_3-C\equiv CH$ (propyne)

Alkyl Halide ⟶ Alkyne

Vicinal dihalide

$CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2}$ $\xrightarrow[\text{dehydrohalogenation, } -HX]{\text{alc KOH}}$ $CH_3-CH=\underset{:\ddot{Cl}:}{CH}$ + H_2O $\xrightarrow[\text{dehydrohalogenation}]{NaNH_2}$ $CH_3-C\equiv CH$ + NH_3

Sodamide (strong base) $Na\ddot{N}H_2$

gem dihalide

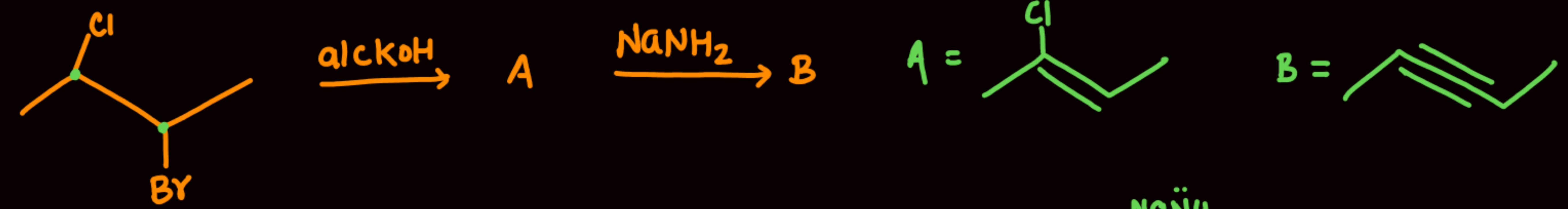
$CH_3-CH_2-CH(Cl)(Cl)$ $\xrightarrow[\text{dehydrohalogenation, } -HX]{\text{alc KOH}}$ $CH_3-CH=CH(:\ddot{Cl}:)$ + H_2O $\xrightarrow[\text{dehydrohalogenation}]{Na\ddot{N}H_2}$ $CH_3-C\equiv CH$ + NH_3

Vicinal tertahalide

$CH_3-CCl_2-CCl_2-H$ $\xrightarrow{2\,Zn\text{-dust}}$ $CH_3-C\equiv CH$

gem - TriHalide

$CH_3-CH_2-CCl_3$ + 6 Ag Powder + $Cl_3C-CH_2-CH_3$ ⟶ $6AgCl + CH_3-CH_2-C\equiv C-CH_2-CH_3$

Eg 

Eg $CH_3-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[\Delta]{\text{alc KOH}} A$

$CH_3-\underset{:\ddot{Br}:}{\underset{|}{C}}=CH-CH_2-CH_3 \xrightarrow{Na\ddot{N}H_2} CH_3-C\equiv C-CH_2-CH_3$

Eg $Ph-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_2 \xrightarrow[\text{(ii) } NaNH_2]{\text{(i) alc KOH}} Ph-C\equiv CH$

Eg $Ph-\overset{Br}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-\overset{Br}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_3 \xrightarrow{2\ Zn\ dust} Ph-C\equiv C-CH_3 + ZnBr_2 + ZnCl_2$

Eg $2\,CH_3-CCl_3 + 6Ag \xrightarrow{\Delta} A$ $\quad CH_3-C\equiv C-CH_3$

Smaller alkyne → Higher alkyne

$$CH_3-C\equiv CH \xrightarrow{RMgX} R-H + CH_3-C\equiv C^{\ominus} \xrightarrow{\overset{\delta+}{CH_3}-\overset{\delta-}{Cl}} CH_3-C\equiv C-CH_3$$

(acidic H; Terminal alkyne) (RMgX: base R^-) (R–H: alkane) (product: non terminal alkyne)

$$CH\equiv CH \xrightarrow{2\,CH_3MgCl} {}^{\ominus}C\equiv C^{\ominus} + 2\,CH_4 \xrightarrow{2\,\overset{\delta+}{CH_3}-Cl} CH_3-C\equiv C-CH_3$$

$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-C\equiv CH \xrightarrow[\text{liq } NH_3]{Na} CH_3-\overset{CH_3}{\overset{|}{C}}H-C\equiv C^{\ominus} \xrightarrow{CH_3-Cl} CH_3-\overset{CH_3}{\overset{|}{C}}H-C\equiv C-CH_3$$

Chemical Reaction of Alkyne

1. Addition of H_2
   X_2/CCl_4
   X_2/H_2O
   HX
   H_2O
2. polymerisation
3. Substitution Reaction
4. oxidation
5. ozonolysis
6. Isomerisation

Addition of H_2

alkyne $\xrightarrow[Ni/Pt/Pd]{H_2}$ alkane

alkyne $\xrightarrow[Pd-C]{H_2}$ alkene

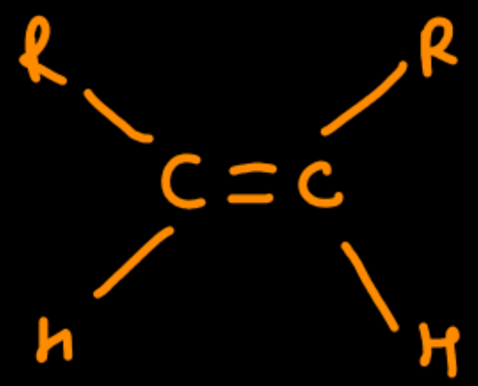
$\xrightarrow[Pd-CaCO_3]{H_2}$ cisalkene } Lindlar's catalyst

$\xrightarrow[Pd-BaSO_4]{H_2}$ " } Rosemund Catalyst

$\xrightarrow[Na, liq NH_3]{H_2}$ Trans alkene } Birch Reduction

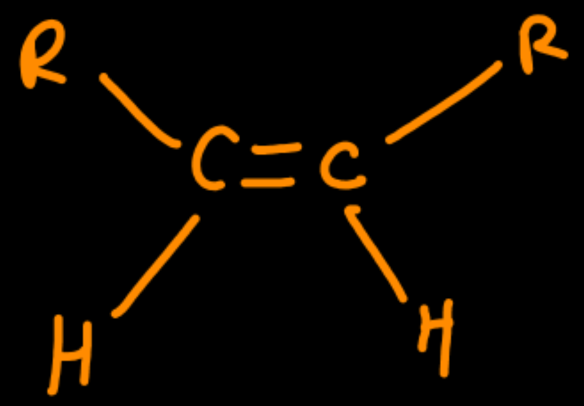
Ques.

$$R-C\equiv C-R \xrightarrow[\text{(CaCO}_3\text{) quino line}]{H_2,\ Pd-C}$$



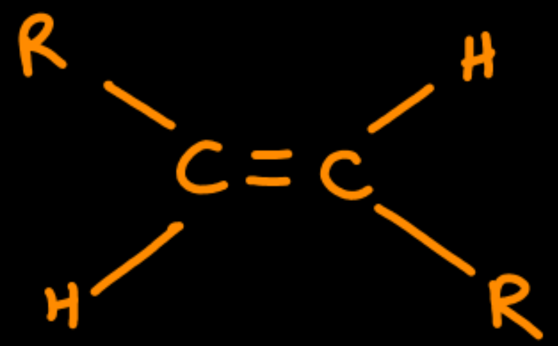
Ques.

$$R-C\equiv C-R \xrightarrow[\text{(BaSO}_4\text{) quino line}]{H_2,\ Pd-C}$$



Ques.

$$R-C\equiv C-R \xrightarrow[\text{Birch reduction}]{\text{Na, Liq.}NH_3}$$



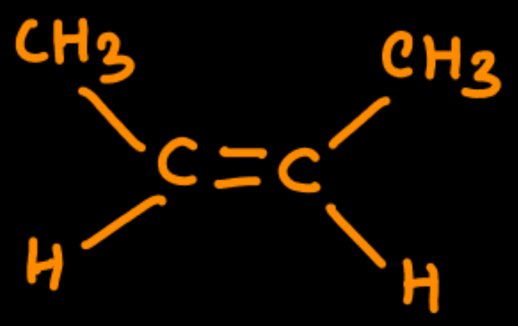
Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[\text{Pt / Pd / Ni}]{H_2}$$

$CH_3-CH_2-CH_2-CH_3$

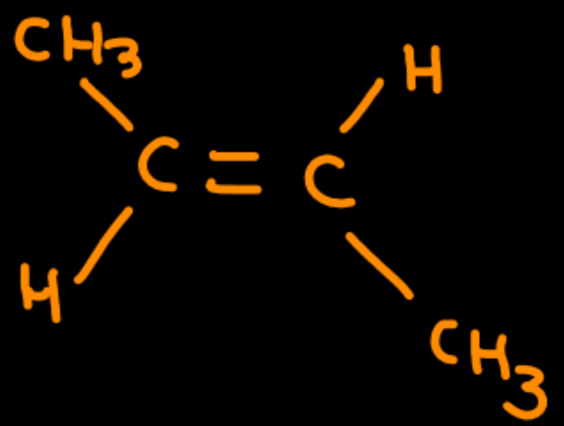
Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2\ /\ Pd,\ BaSO_4\ /\ CaCO_3]{\text{Rosenmund Catalyst or Lindiar's catalyst}}$$

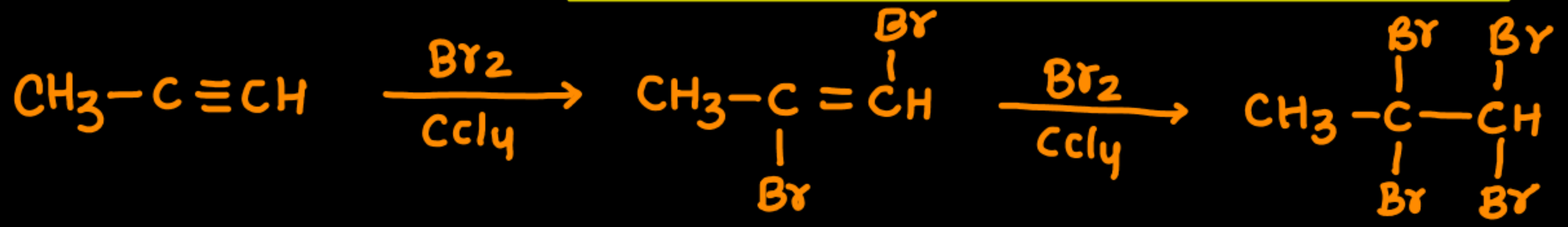


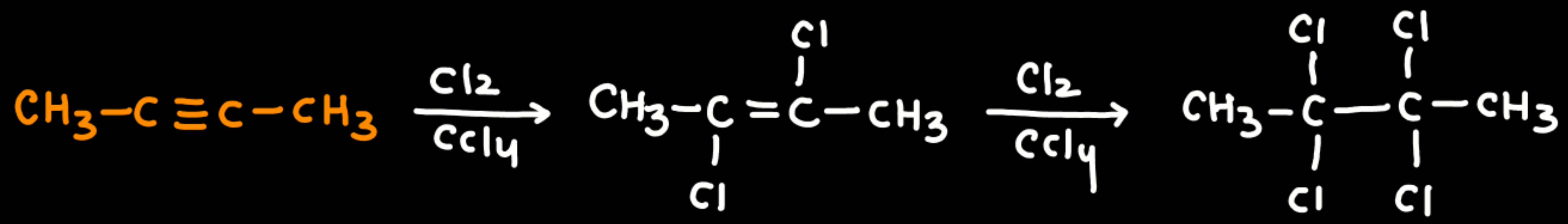
Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[Pt\ /\ Liq.NH_3]{\text{Birch reduction}}$$



Alkyne ⟶ Addition of X_2





Ques.

✓ $CH_3-C\equiv CH \xrightarrow[CCl_4]{Br_2}$

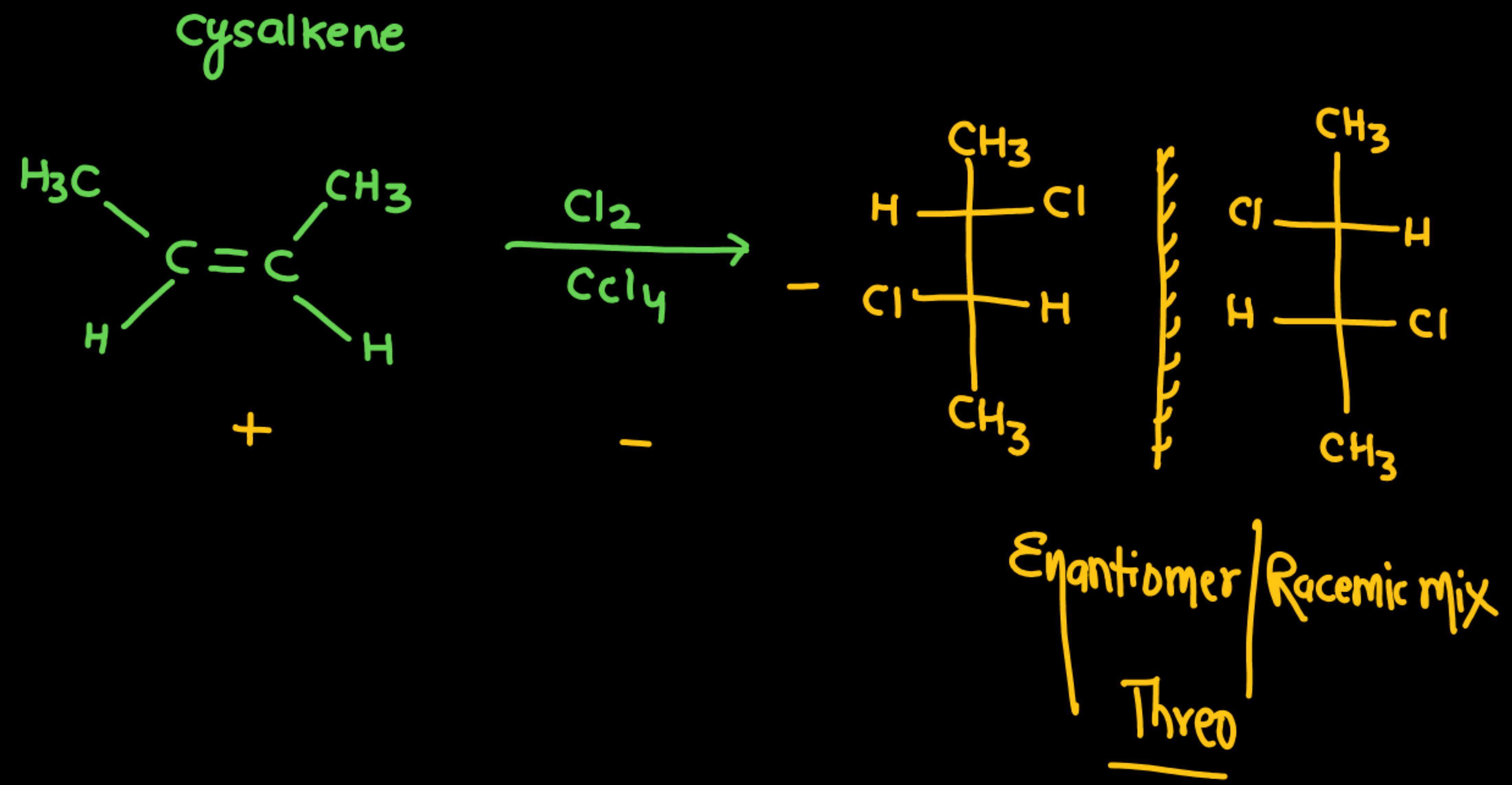
Ques.

✓ $CH_3-C\equiv C-CH_3 \xrightarrow[CCl_4]{Br_2}$

Find out the structure of A and B in the following reaction:

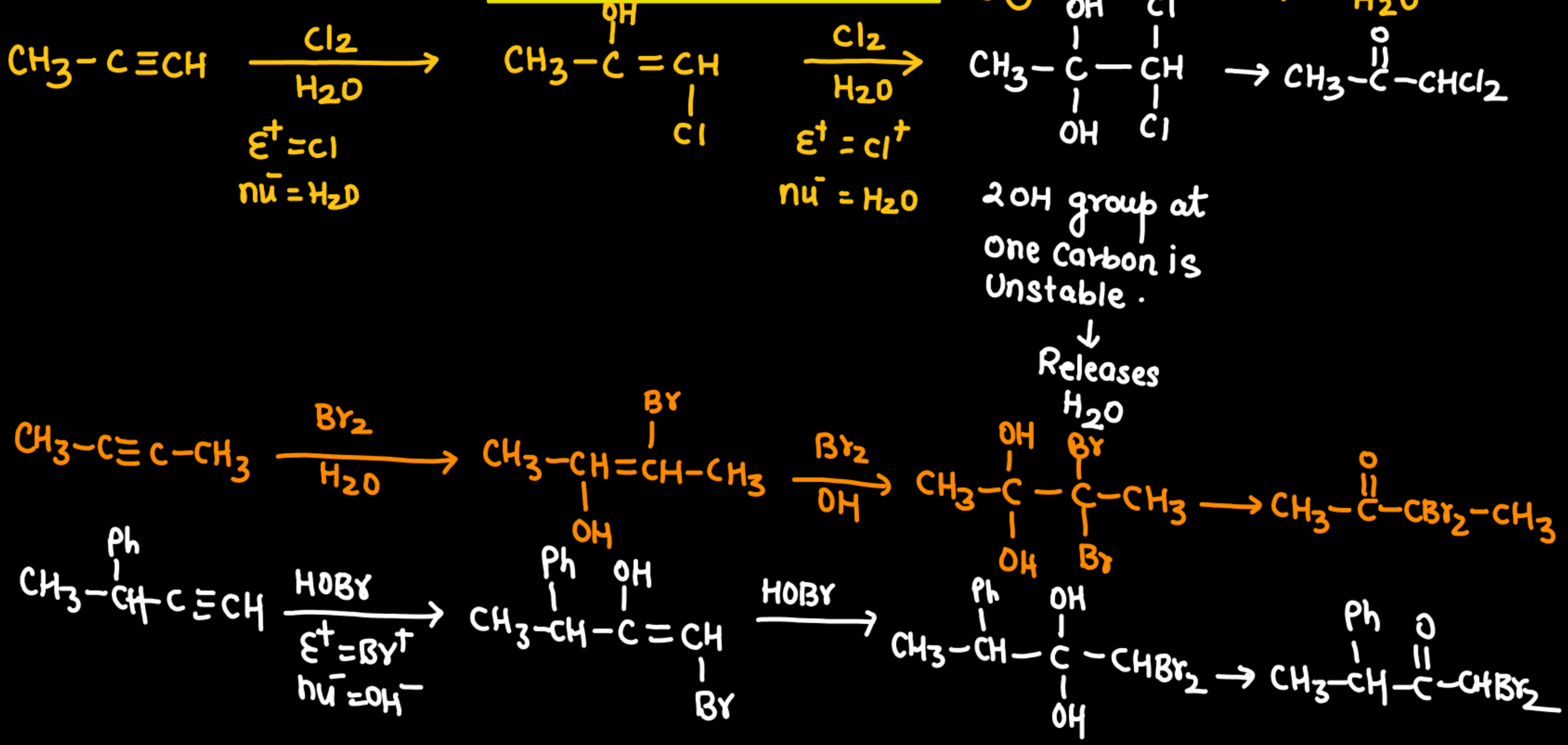
Ques.

$$H_3C-C\equiv C-CH_3 + H_2 \xrightarrow{Pd\ /\ CaCO_3} A \xrightarrow{Cl_2\ /\ CCl_4} B$$



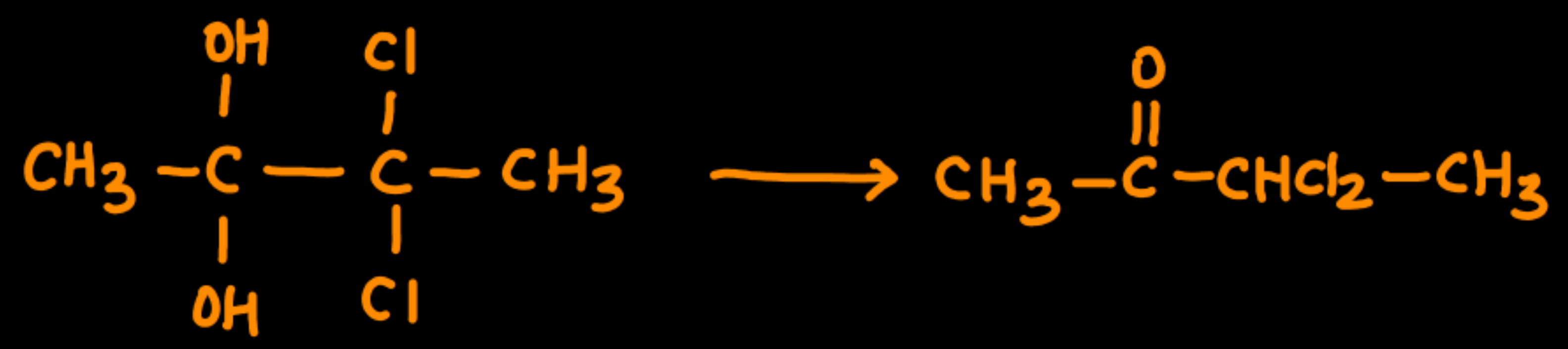
Addition of HoX

(Hypohalousacid) $\xrightarrow[H_2O]{X_2}$



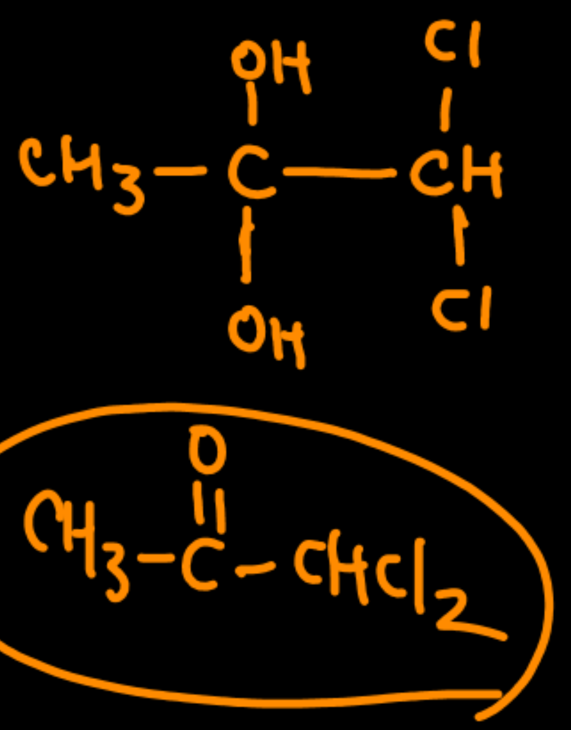
Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[Cl^+ \; OH^-]{HoCl}$$



Ques.

$$CH_3-C\equiv CH \xrightarrow[Cl^+ \; OH^-]{HoCl}$$



Addition of H_2O

(I)

$$R-C\equiv CH \xrightarrow[40\%\ H_2SO_4]{1\%\ HgSO_4} \underset{\text{enol}}{R-\overset{\overset{1}{OH}}{\underset{2}{C}}=\underset{3}{CH_2}} \underset{\text{Tautomer}}{\rightleftharpoons} R-\overset{\overset{O}{\|}}{C}-CH_3 \quad \text{(Markovnikov Rule)}$$

or

$$\xrightarrow{Hg^{+2}/H^{+}}$$

(II)

$$R-C\equiv CH \xrightarrow[H_2O_2/OH^-]{BH_3/THF} \underset{\text{enol}}{R-CH=\underset{OH}{CH_2}} \underset{\text{Tautomer}}{\rightleftharpoons} R-CH_2-\underset{\underset{O}{\|}}{C}-H \quad \text{(antimarkovnikov Rule)}$$

(HBO)

(HydroBoration oxidation)

Ques.

$$CH_3-C\equiv CH \xrightarrow[\text{dil.}H_2SO_4]{Hg^{2+}} \text{MK Rule}$$

$$CH_3-\underset{}{\overset{OH}{C}}=CH_2 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Ques.

$$CH_3-C\equiv CH \xrightarrow[H_2O_2\ /\ OH^-]{BH_3\ /\ THF} \text{AMK Rule}$$

$$CH_3-CH=\underset{OH}{CH} \rightleftharpoons CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H$$

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[\text{dil.}H_2SO_4]{Hg^{2+}} CH_3-\underset{}{\overset{OH}{\overset{|}{C}}}=CH-CH_3 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2O_2\ /\ OH^-]{BH_3\ /\ THF} CH_3-\overset{OH}{\overset{|}{C}}=CH-CH_3 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

Ques.

$$CH_3-CH_2-C\equiv CH \xrightarrow[\text{dil.}H_2SO_4]{Hg^{2+}} \text{MK}$$

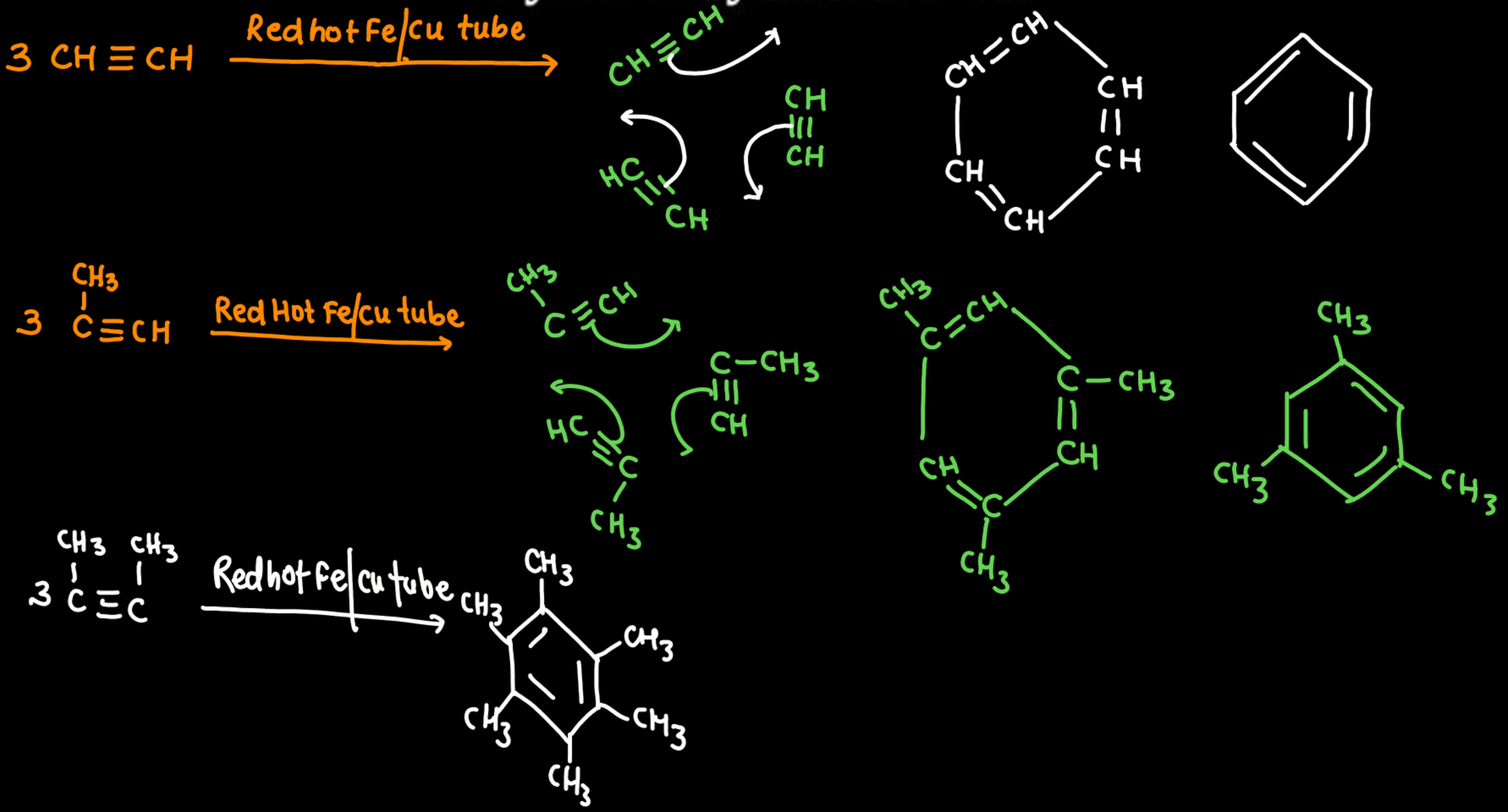
$$CH_3-CH_2-\underset{}{\overset{OH}{\overset{|}{C}}}=CH_2 \rightleftharpoons CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_3$$

Ques.

$$CH_3-CH_2-C\equiv CH \xrightarrow[H_2O_2\ /\ OH^-]{BH_3\ /\ THF} \text{AMK}$$

$$CH_3-CH_2-CH=\underset{OH}{\underset{|}{CH}} \rightleftharpoons CH_3-CH_2-CH_2-\underset{O}{\underset{||}{C}}-H$$

Cyclic Polymerization



Ques.

$$3\ CH\equiv CH \xrightarrow[\text{quartz tube (873 K)}]{\text{Red hot Fe, Cu,}}$$

Ques.

$$3\ CH_3-C\equiv H \xrightarrow[\text{quartz tube (873 K)}]{\text{Red hot Fe, Cu,}}$$

Ques.

$$3\ CH_3-C\equiv C-CH_3 \xrightarrow[\text{quartz tube (873 K)}]{\text{Red hot Fe, Cu,}}$$

Substitution Reaction

$$CH \equiv CH \xrightarrow[\text{(base)}]{\text{Na metal}} CH \equiv C^{\ominus}Na^{+} + \frac{1}{2}H_2 \xrightarrow[\text{(base)}]{\text{Na metal}} Na^{+}\,{}^{\ominus}C \equiv C^{\ominus}\,Na^{+} + \frac{1}{2}H_2$$

Sodium acetylide or Sodium ethynide

disodium acetylide or disodium ethynide

$$CH \equiv CH \xrightarrow[\text{Strong base}]{NaNH_2} CH \equiv C^{\ominus}\,Na^{\oplus} + NH_3 \xrightarrow{NaNH_2} Na^{+}\,{}^{-}C \equiv C^{-}\,Na^{+} + NH_3$$

Sodium acetylide

disodium acetylide

$$R-C \equiv C-H + \underline{CuCl_2 + NH_4OH} \longrightarrow (R-C \equiv C^{\ominus})_2Cu^{+2}$$

Ammonical cupric chloride

Red ppt

$$R-C \equiv C-H + AgNO_3 + NH_4OH \longrightarrow R-C \equiv C^{\ominus}Ag^{+}$$

Ammonium silver nitrate (Tollen's Regent)

White ppt

Substitution Reaction

$$CH \equiv CH \xrightarrow[\text{(base)}]{Na \text{ metal}} CH \equiv C^{\ominus} Na^{+} + \frac{1}{2} H_2 \xrightarrow[\text{(base)}]{Na \text{ metal}} Na^{+} \, {}^{\ominus}C \equiv C^{\ominus} \, Na^{+} + \frac{1}{2} H_2$$

Sodium acetylide or Sodium ethynide → disodium acetylide or disodium ethynide

$$CH \equiv CH \xrightarrow[\text{Strong base}]{NaNH_2} CH \equiv C^{\ominus} Na^{\oplus} + NH_3 \xrightarrow{NaNH_2} Na^{+} \, {}^{-}C \equiv C^{-} \, Na^{+} + NH_3$$

Sodium acetylide → disodium acetylide

$$R-C \equiv C-H + CuCl_2 + NH_4OH \longrightarrow (R-C \equiv C^{\ominus})_2 Cu^{+2}$$

Ammonical cupric chloride → Red ppt

$$R-C \equiv C-H + AgNO_3 + NH_4OH \longrightarrow R-C \equiv C^{\ominus} Ag^{+}$$

Ammonium silver nitrate (Tollen's Regent) → White ppt

Oxidation Reaction

Ques.

$$CH_3-C\equiv C-H \xrightarrow[Br\ H^+ / K_2Cr_2O_7]{H^+ / KMnO_4}$$

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[Br\ H^+ / K_2Cr_2O_7]{H^+ / KMnO_4}$$

Oxidation with alkaline $KMnO_4$ (Bayer's reagent)

Ques.

$$CH \equiv CH \xrightarrow{\text{alk. } KMnO_4}$$

Ques.

$$CH_3-C \equiv CH \xrightarrow{\text{alk. } KMnO_4}$$

Ques.

$$CH_3-C \equiv C-CH_3 \xrightarrow{\text{alk. } KMnO_4}$$

Oxidation by Selenium oxide (SeO_2)

Ques.

$$CH\equiv CH \xrightarrow{SeO_2}$$

Ques.

$$CH_3-C\equiv CH \xrightarrow{SeO_2}$$

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow{SeO_2}$$

Ozonolysis

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[ZnH_2O]{O_3}$$

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2O]{O_3}$$

Isomerization

Ques.

$$R-CH_2-C\equiv CH \xrightarrow{\text{alc.KOH}}$$

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow{NaNH_2}$$

In absence of Zinc, Ozonolysis followed by hydrolysis produces acid.

Ques.

$$CH_3{-}CH_2{-}C{\equiv}C{-}H \xrightarrow[H_2O]{O_3}$$

THANK YOU

All the Best!! 👍

Oxidation Reaction

① $H^+/KMnO_4$ & H^+/Cr_2O_7 — Strong Oxidising Agent { Break π bond & add oxygen. }

② Bayer's Reagent (alkaline $KMnO_4$) → addition of 'OH'. (Mild oxidising Agent)
(Cold $KMnO_4$)

Ques.

$$CH_3-C\equiv C-H \xrightarrow[\text{Or } H^+/K_2Cr_2O_7]{H^+/KMnO_4} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + H-\overset{O}{\overset{\|}{C}}-OH$$

Strong oxidizing agent

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[\text{Or } H^+/K_2Cr_2O_7]{H^+/KMnO_4} 2\,CH_3-\overset{O}{\overset{\|}{C}}-OH$$

$$\xrightarrow{D^+/KMnO_4} 2\,CH_3-\overset{O}{\overset{\|}{C}}-OD$$

Oxidation with alkaline $KMnO_4$ (Bayer's reagent) (Pink color)

Ques.

$$CH\equiv CH \xrightarrow[\text{(pink color)}]{\text{alk. } KMnO_4} H-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-H$$

OH OH

OH OH

(Colorless)

Ques.

$$CH_3-C\equiv CH \xrightarrow[\text{(pink color)}]{\text{alk. } KMnO_4} CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-H$$

(Colorless)

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[\text{(pink color)}]{\text{alk. } KMnO_4} CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-CH_3$$

Colorless

Oxidation by Selenium oxide (SeO_2) → Same as Bayer's Reagent

Ques.

$$CH\equiv CH \xrightarrow{SeO_2} H-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-H$$

Ques.

$$CH_3-C\equiv CH \xrightarrow{SeO_2} CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-H$$

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow{SeO_2} CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-CH_3$$

Ozonolysis

① Reductive ozonolysis $\xrightarrow[Zn,\ H_2O]{O_3}$

② oxidative ozonolysis $\xrightarrow[H_2O]{O_3}$

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[Zn, H_2O]{O_3} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

Reductive ozonolysis

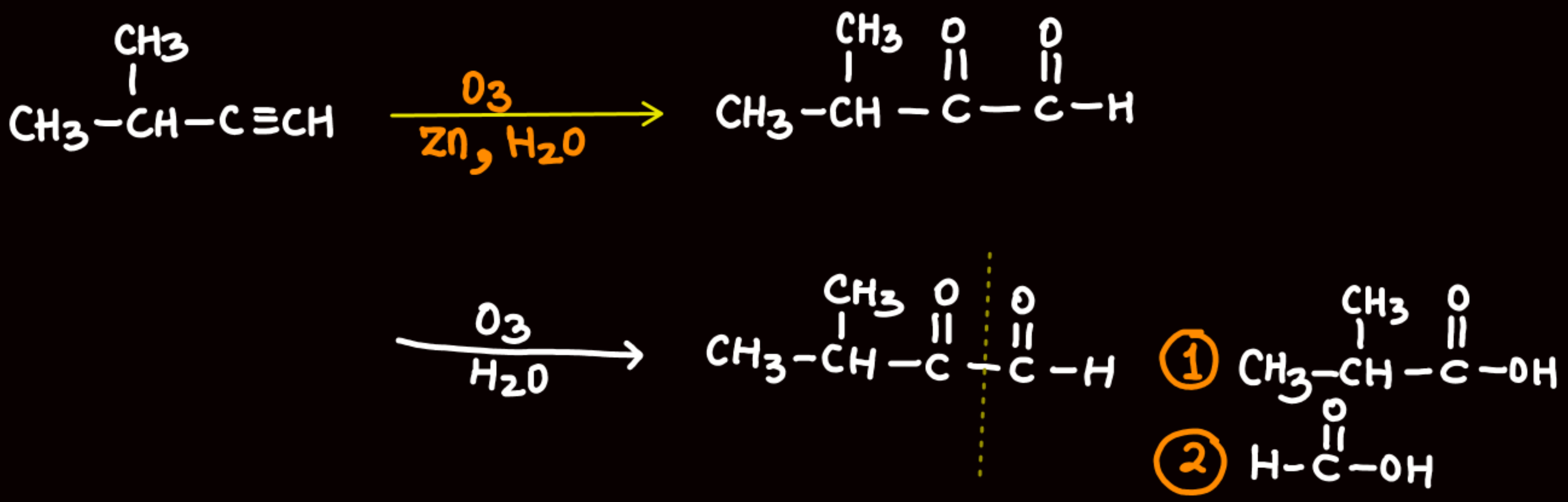
Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2O]{O_3} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

oxidative ozonolysis (H_2O_2)

$$CH_3-\overset{O}{\overset{\|}{C}}-OH$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH$$


CH3
CH3−CH−C≡CH
O3
Zn, H2O
CH3 O O
CH3−CH−C−C−H
O3
H2O
1 CH3−CH−C−OH
2 H−C−OH

Method of Preparation of Benzene

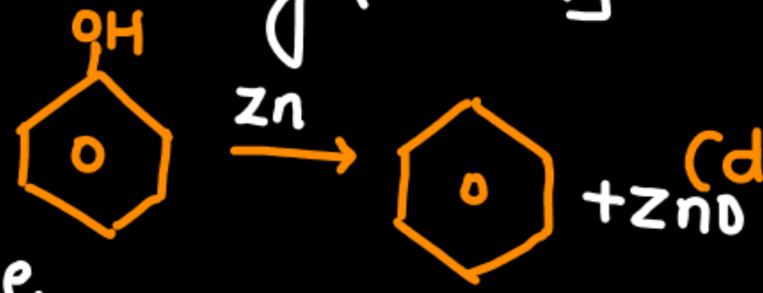
① Alkane → Benzene [Aromatisation]

② Alkyne → Benzene [cyclic polymerisation]

③ Aryl Halide → Benzene [Fittig Reaction]

[Wurtz Fittig Reaction]

④ phenol ⟶ Benzene



(deoxygenation)

⑤ Aldehyde/ketone → Benzene

Basic Med. (i) Wolf Kishner Reduction
Acidic Med. (ii) Clemmenson Reduction

} Remove 'O'. add 'H'.

⑥ Carboxylic acid $\xrightarrow[\text{lime}]{\text{soda}}$ Benzene

decarboxylation

(i) Carbanion

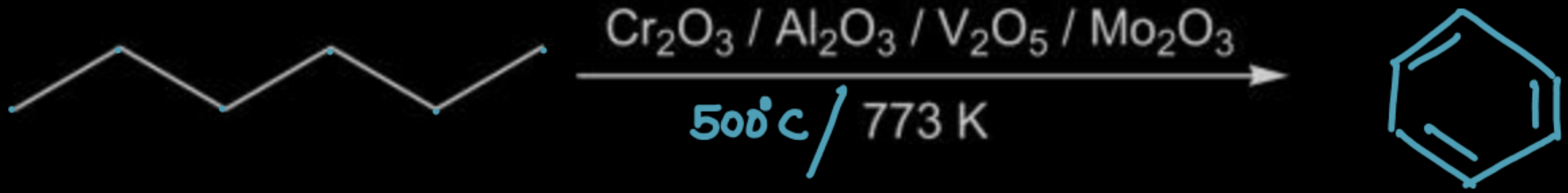
⑦ Grignard ⟶ Benzene

⑧ Benzenediazonium Salt ⟶ Benzene

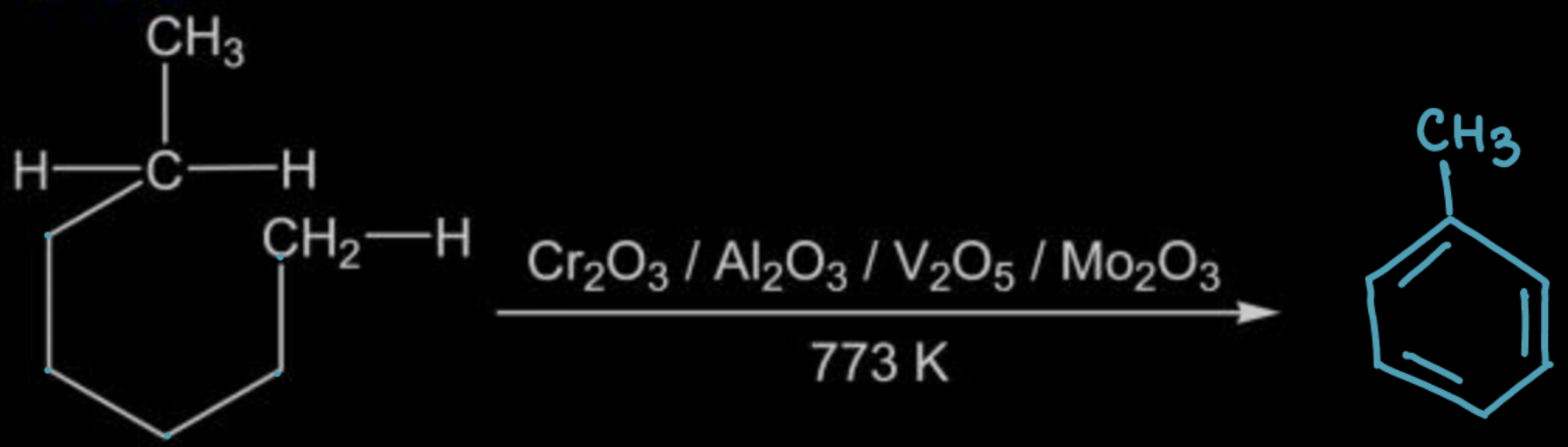
Method of Preparation: -

(I) From Alkane:

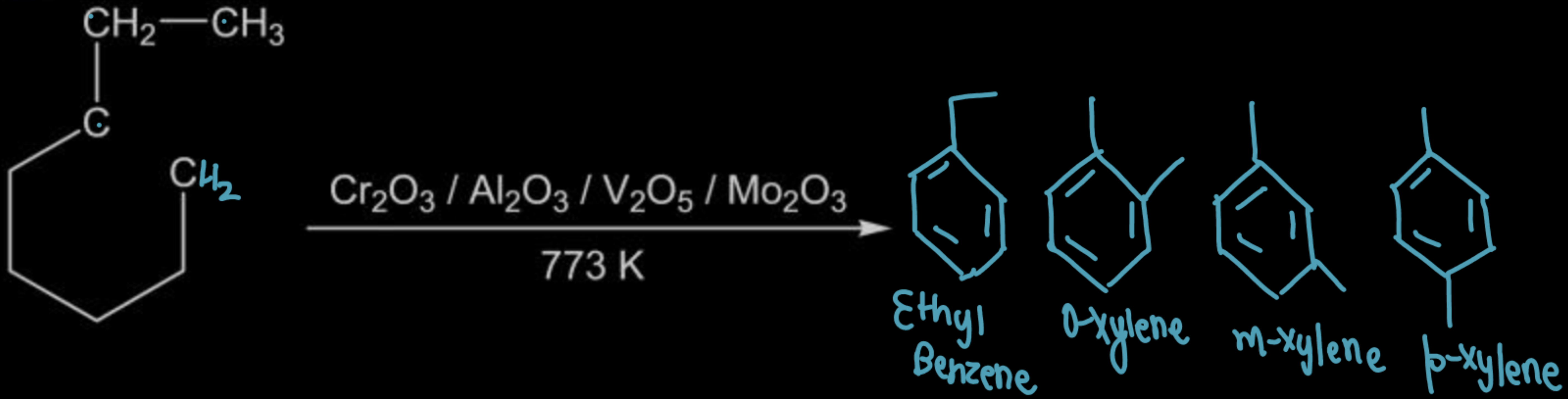
Ques.



Ques.


CH3
H—C—H
CH2—H
Cr2O3 / Al2O3 / V2O5 / Mo2O3
773 K
CH3

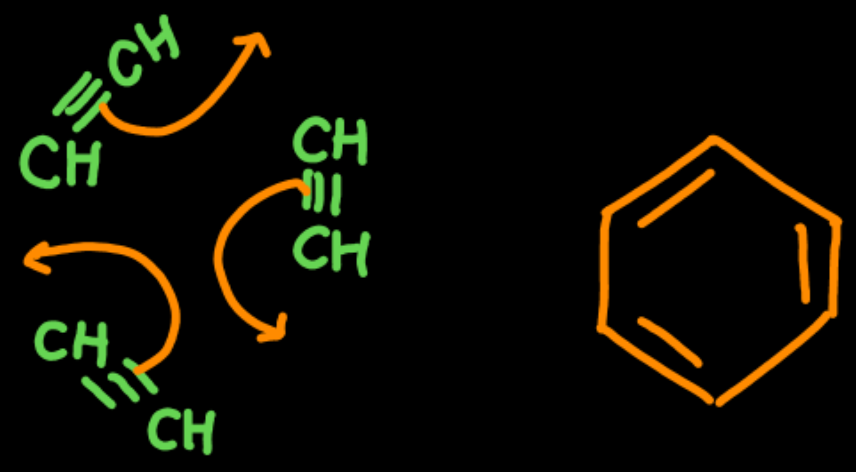
Ques.


CH2—CH3
C
CH2
Cr2O3 / Al2O3 / V2O5 / Mo2O3
773 K
Ethyl Benzene
o-xylene
m-xylene
p-xylene

(II) From Alkyne:

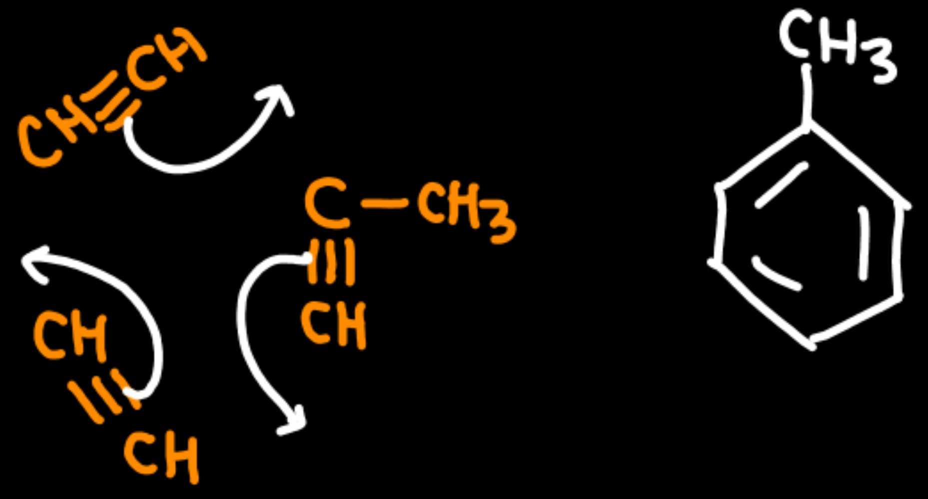
Ques.

$$3\ HC\equiv CH \xrightarrow[(500-600^\circ C)]{\text{Red hot Fe, Cu tube}}$$



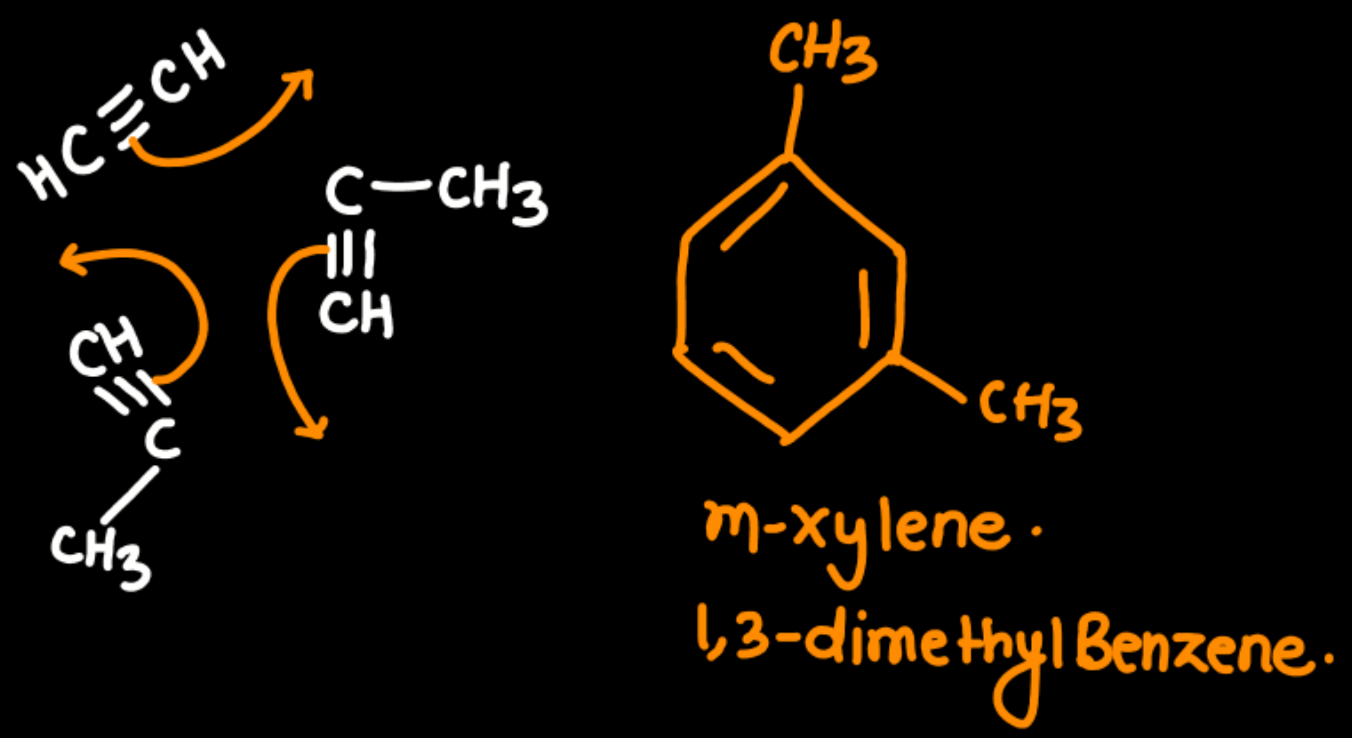
Ques.

$$2\ HC\equiv CH + H_3C-C\equiv CH \xrightarrow[(500-600^\circ C)]{\text{Red hot Fe, Cu tube}}$$



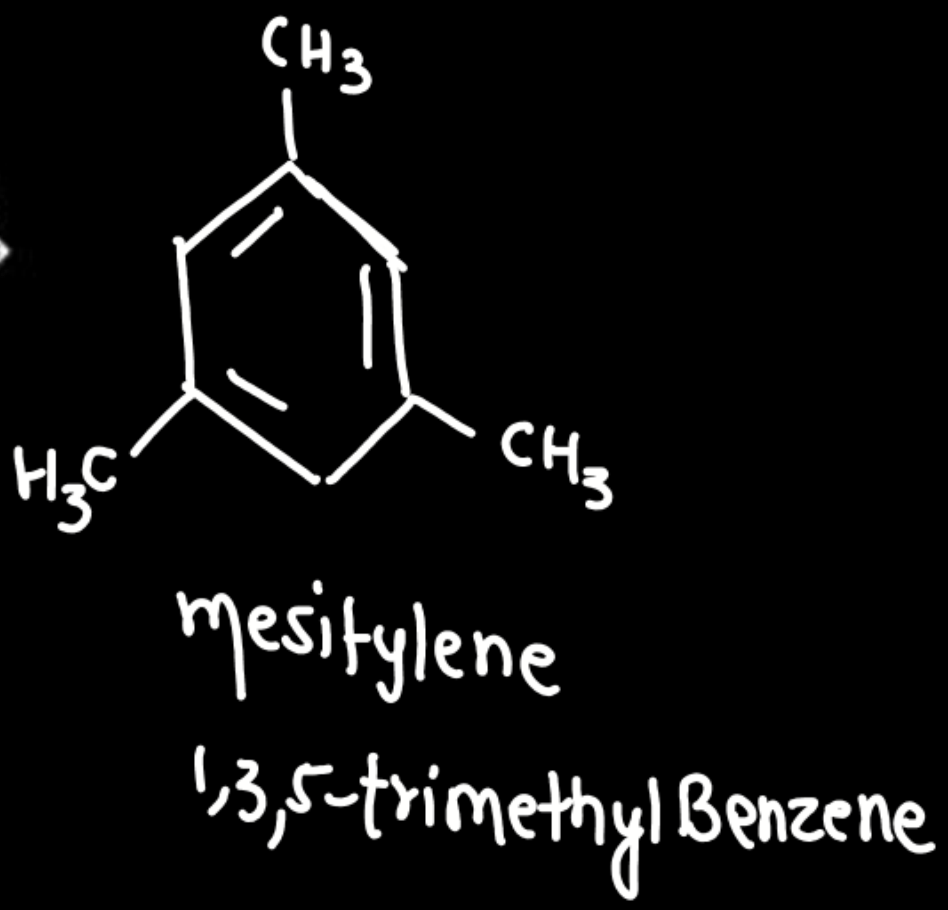
Ques.

$$2\,H_3C{-}C{\equiv}CH + HC{\equiv}CH \xrightarrow[(500-600^\circ C)]{\text{Red hot Fe, Cu tube}}$$



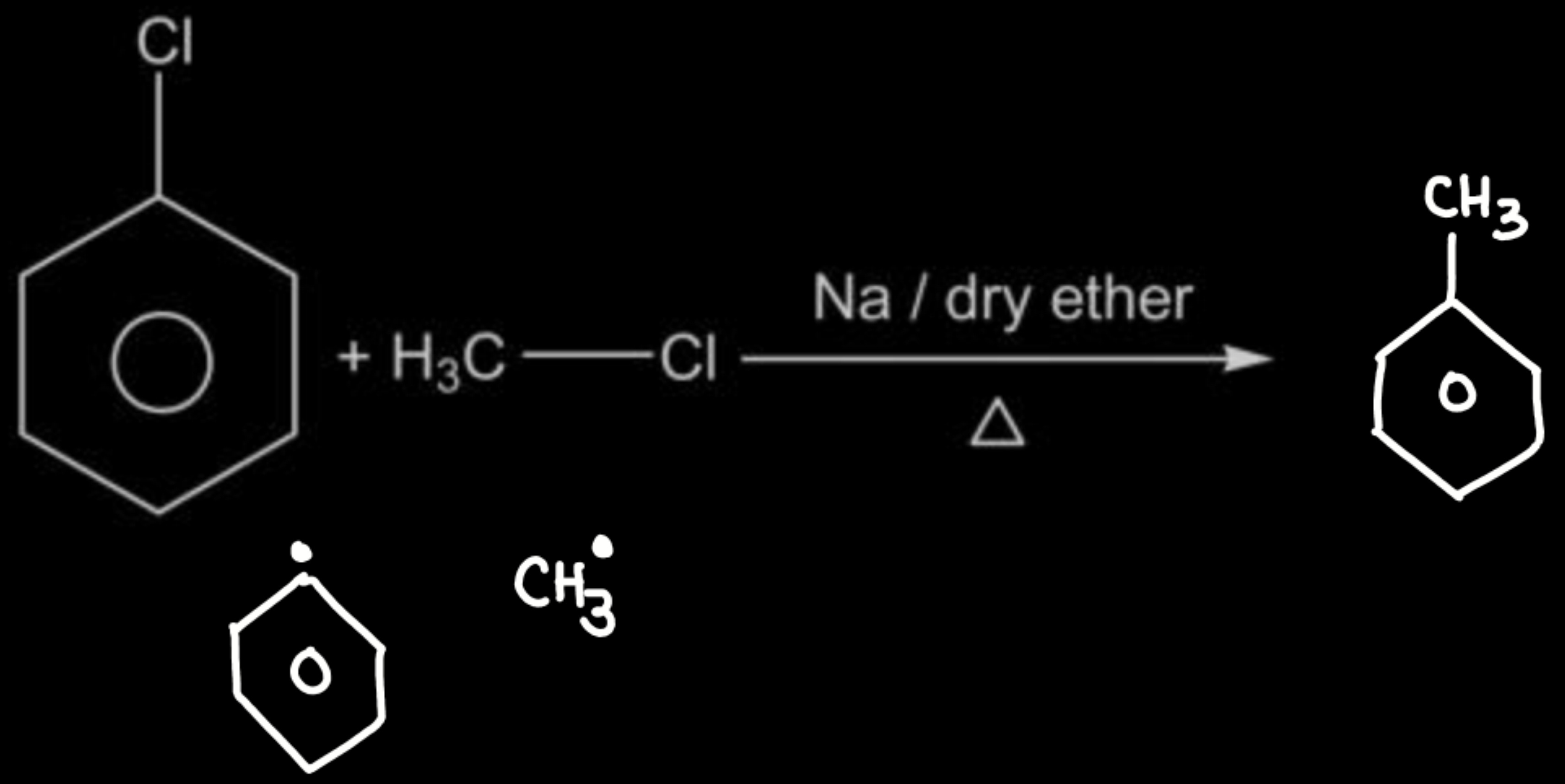
Ques.

$$3\,H_3C{-}C{\equiv}CH \xrightarrow[(500-600^\circ C)]{\text{Red hot Fe, Cu tube}}$$

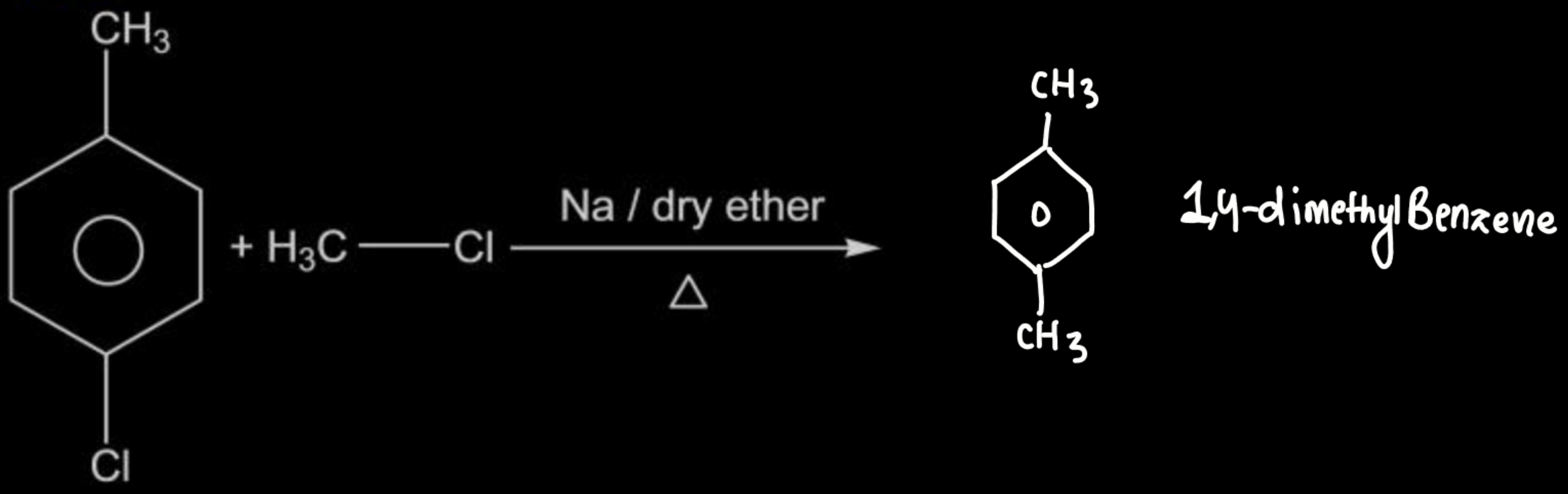


(III) From Alkyl Halide:

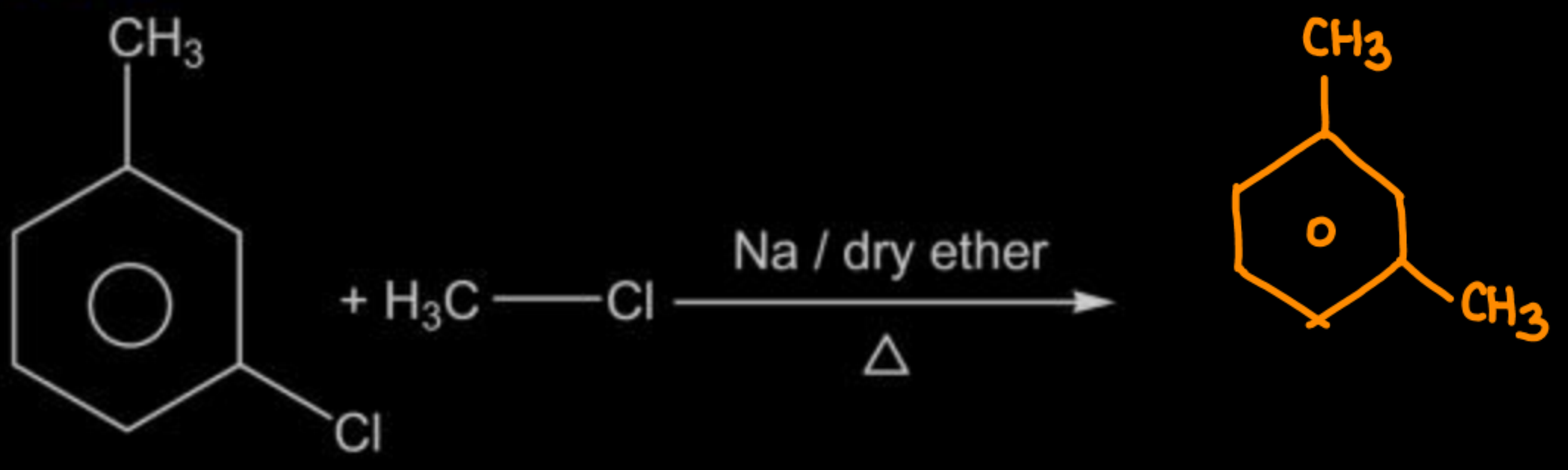
Ques. Wurtz-Fittig Reaction



Ques.

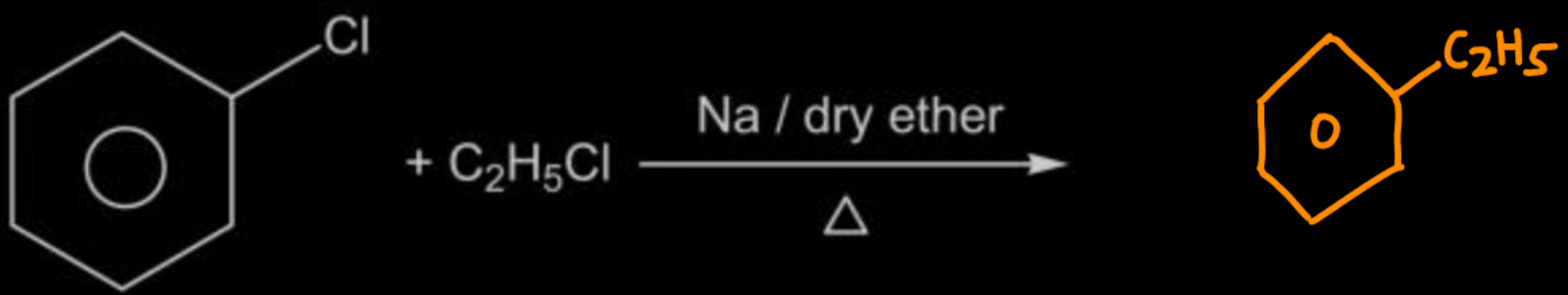


Ques.



CH3
Cl
+ H3C—Cl
Na / dry ether
Δ
CH3
CH3

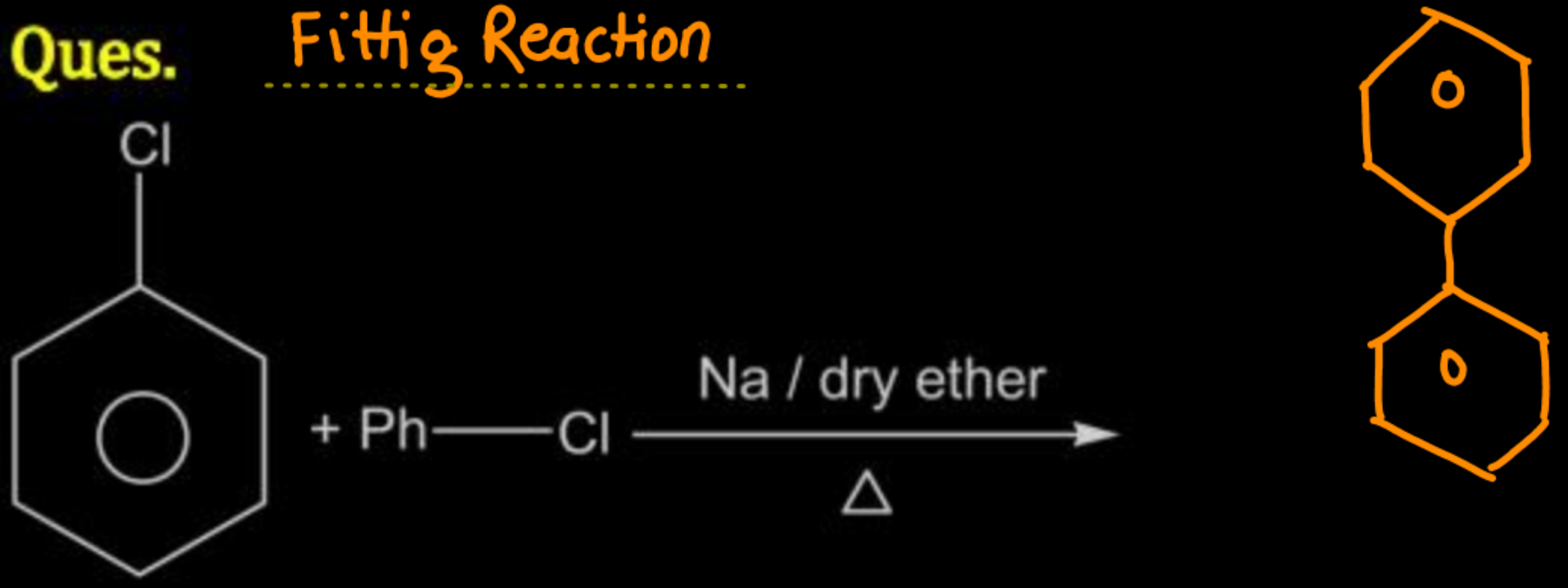
Ques.



Cl
+ C2H5Cl
Na / dry ether
Δ
C2H5

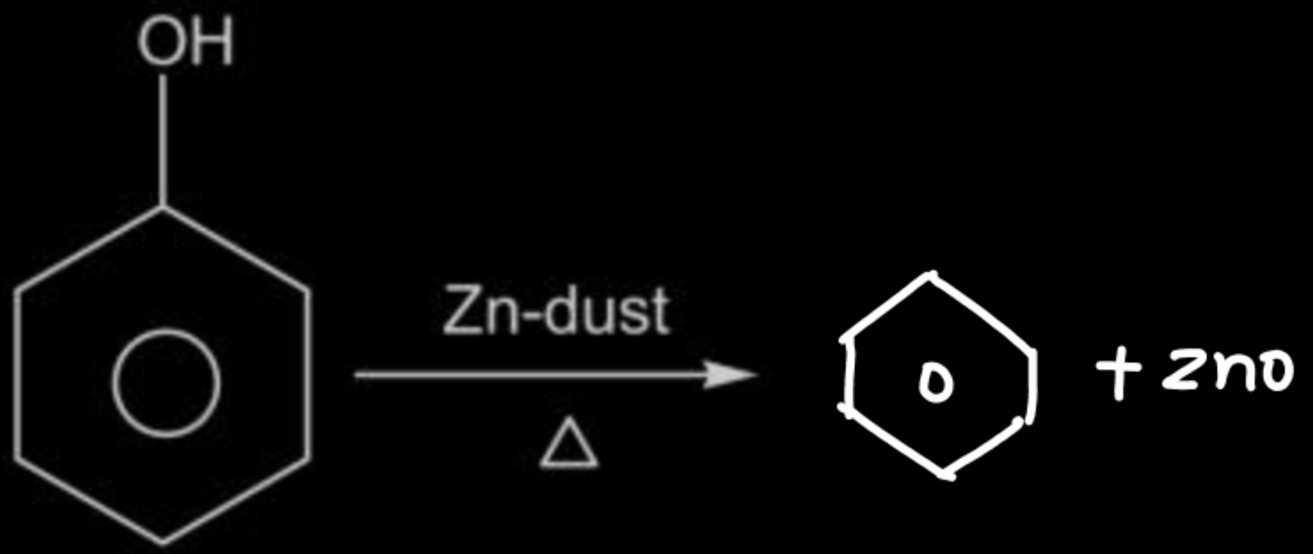
PACPCH

Ques. Fittig Reaction

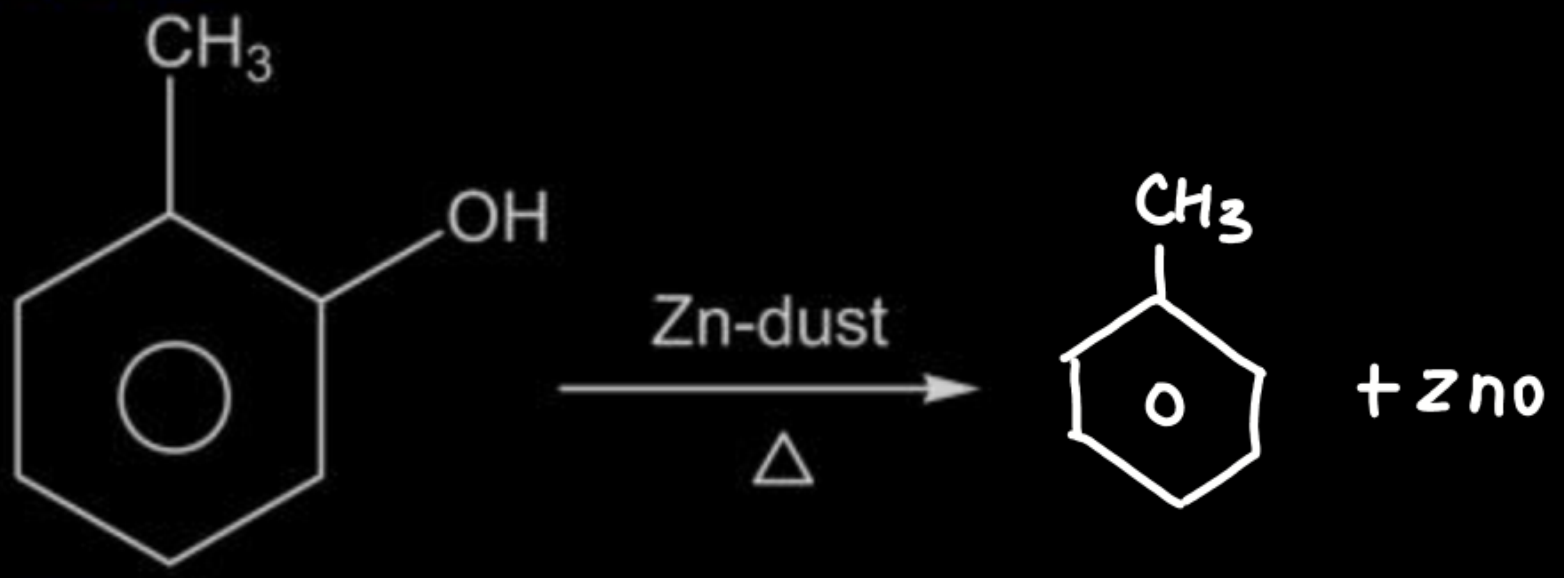


(IV) Phenol by Reduction:

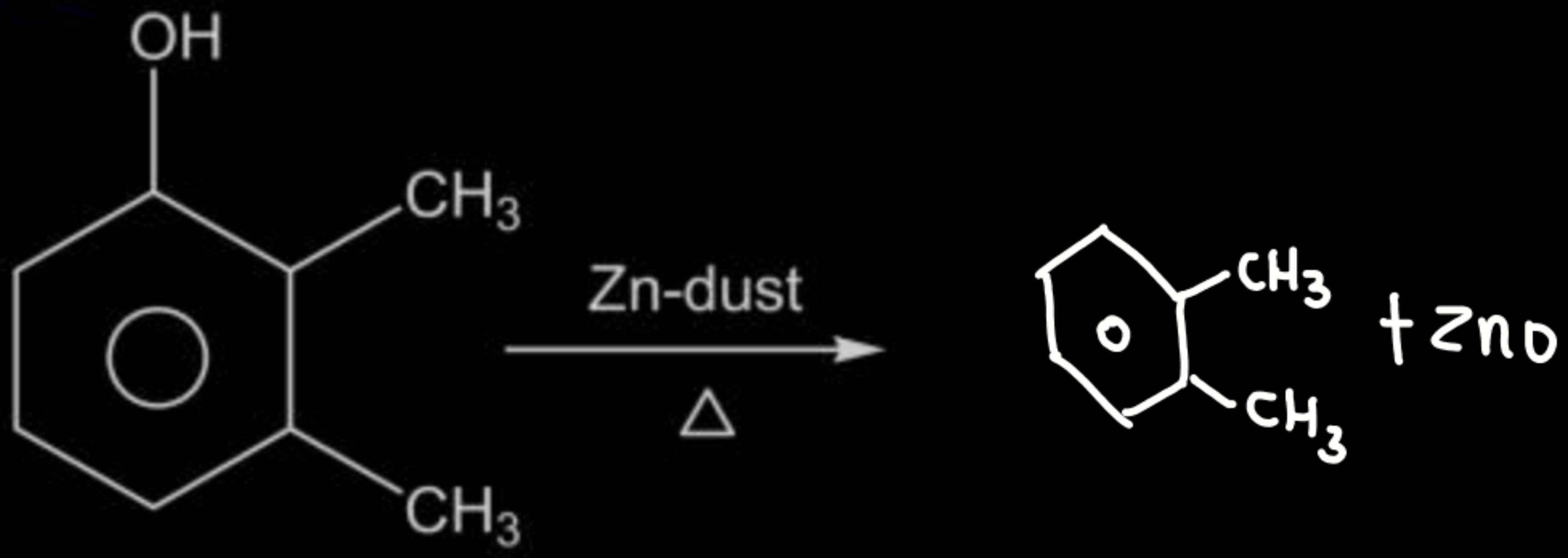
Ques.



Ques.

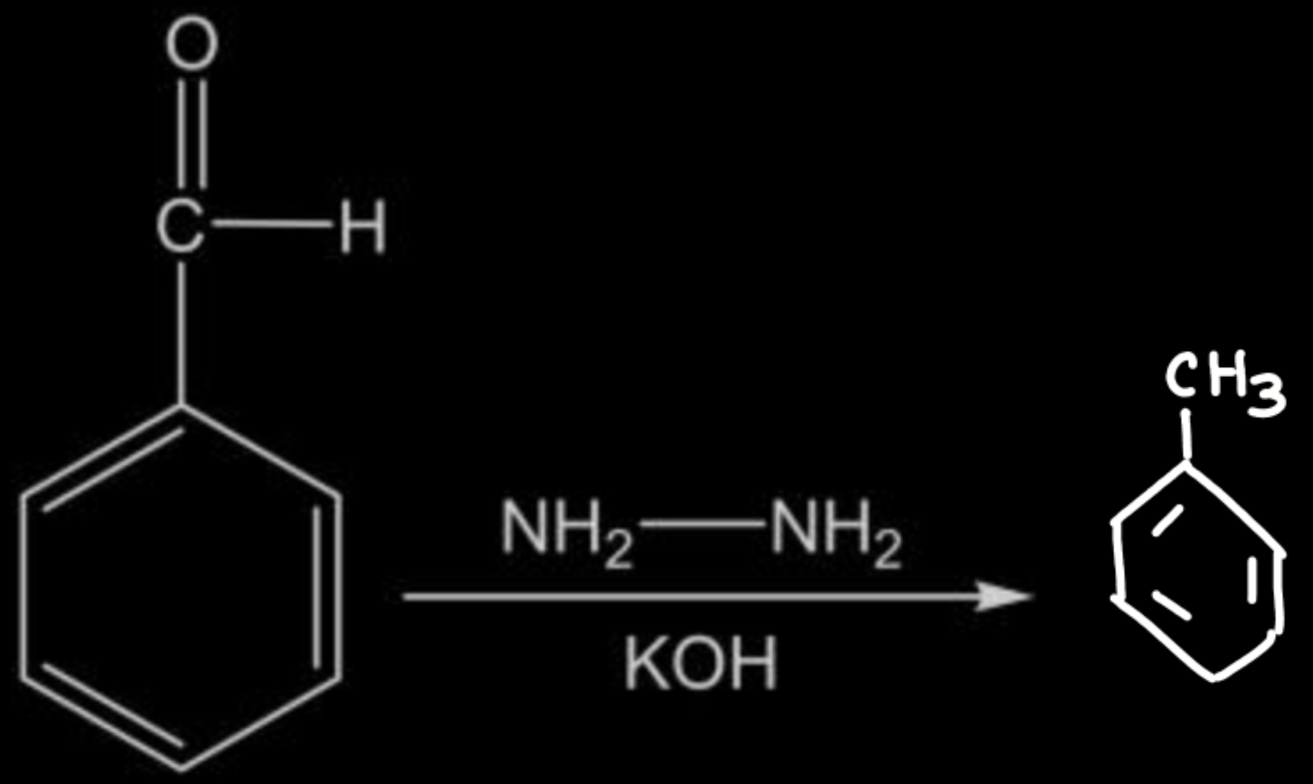


Ques.

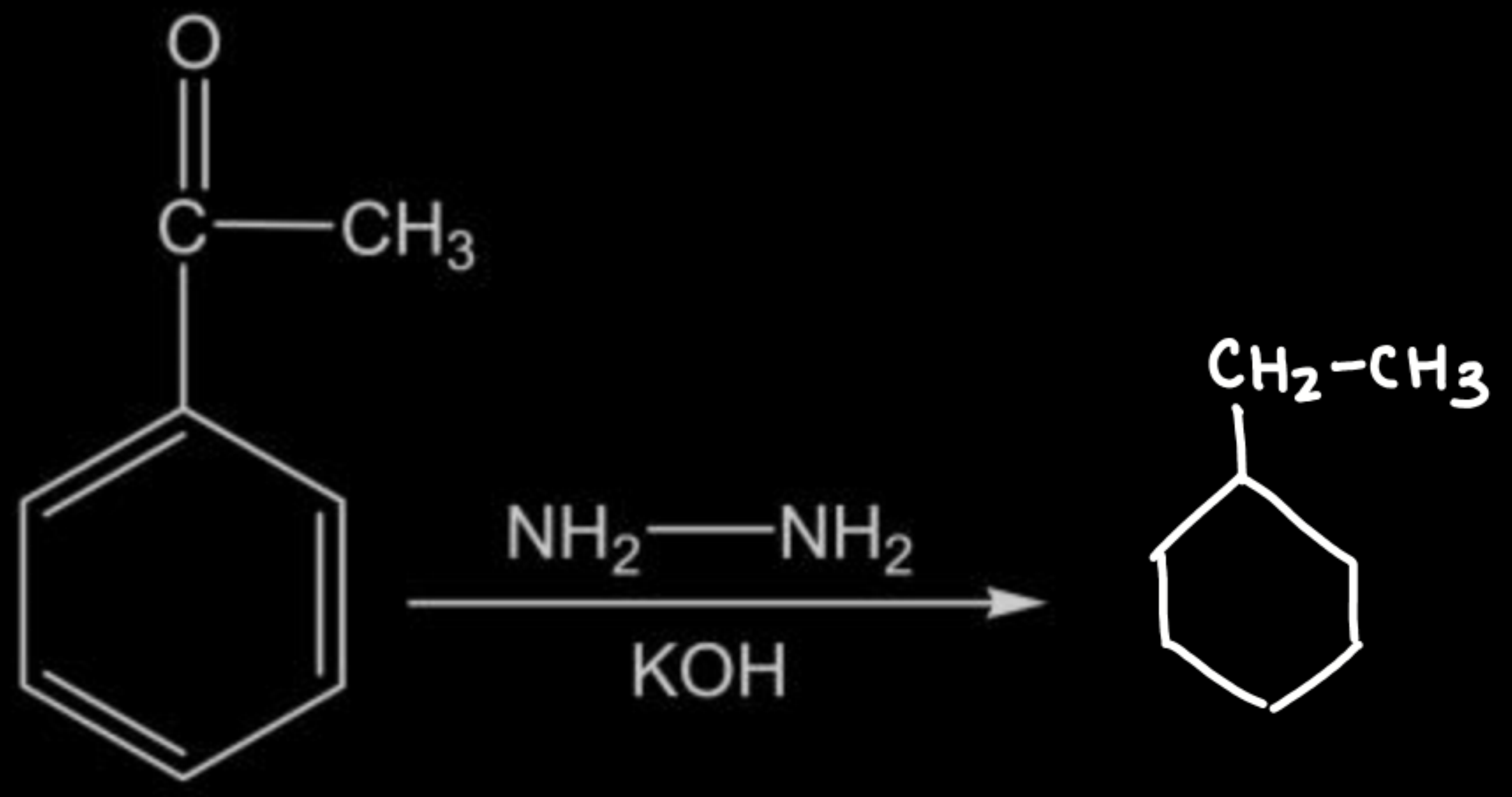


Wolf-Kishner Reaction:

Ques.

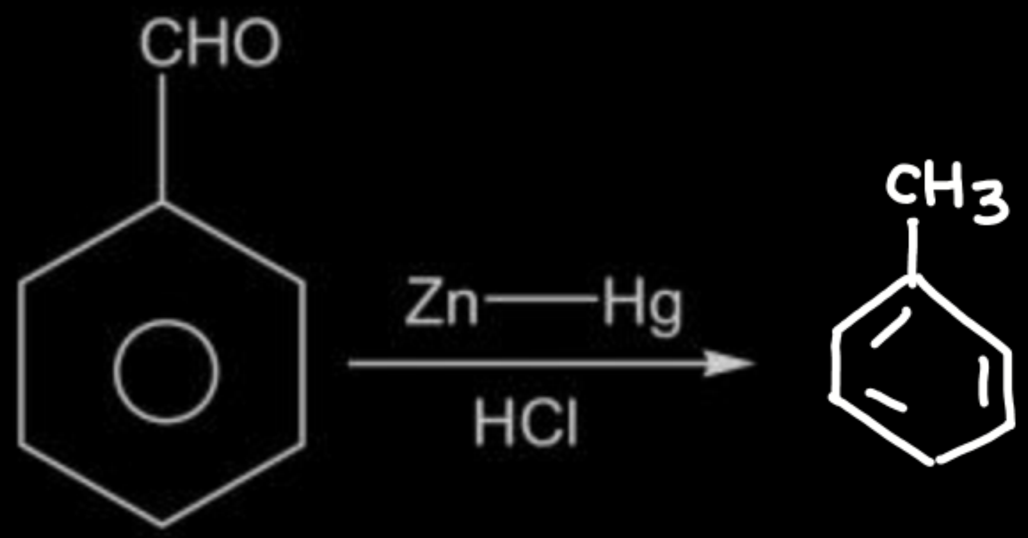


Ques.

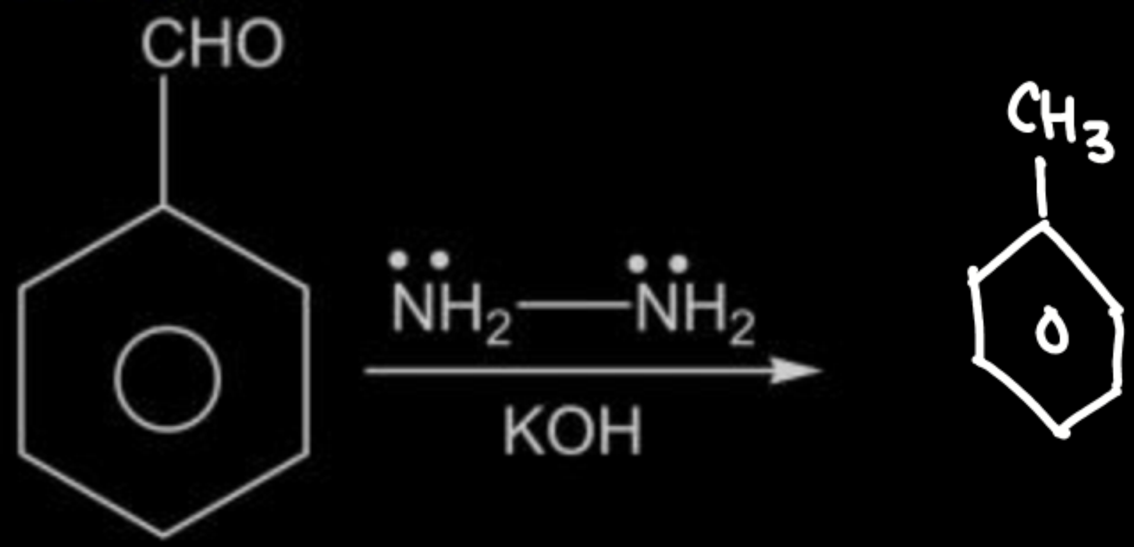


(V) From Aldehyde/Ketone:

Ques.

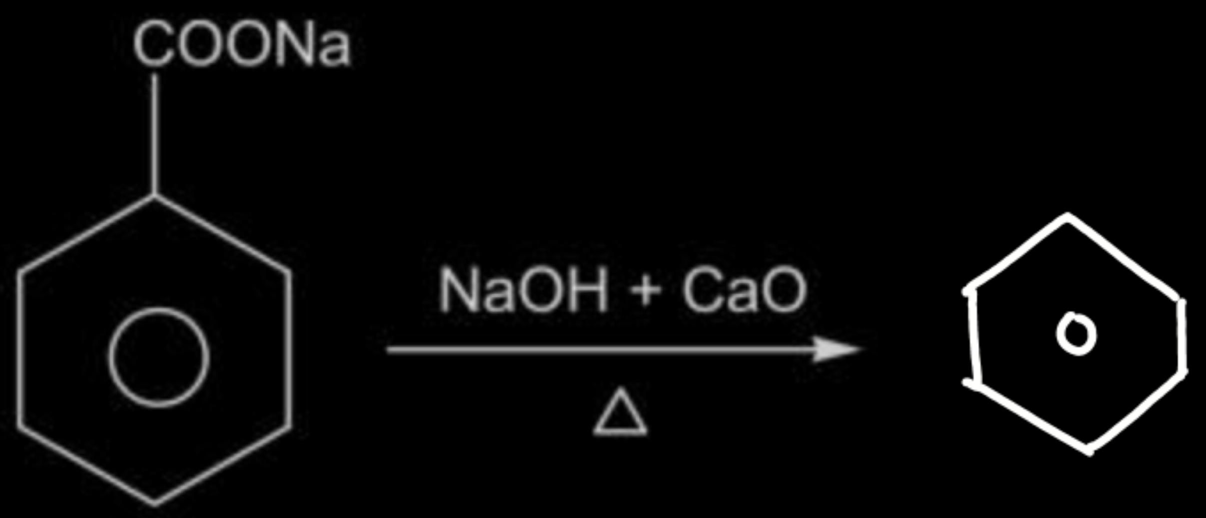


Ques.

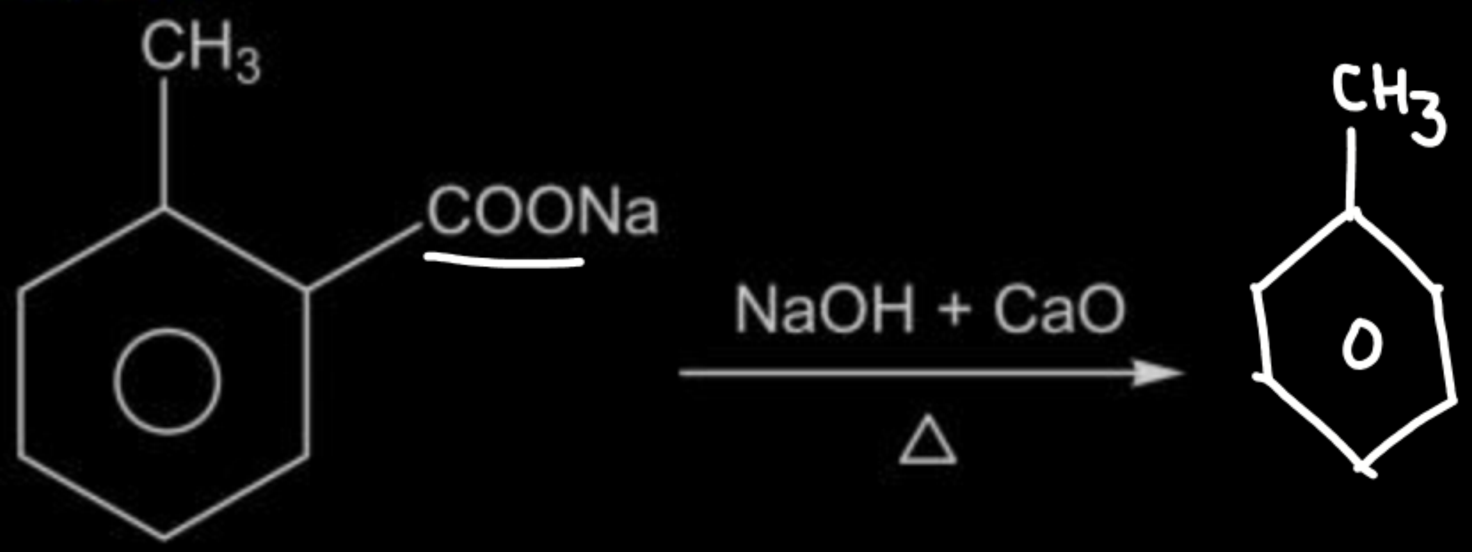


(VI) From Carboxylic Acid:

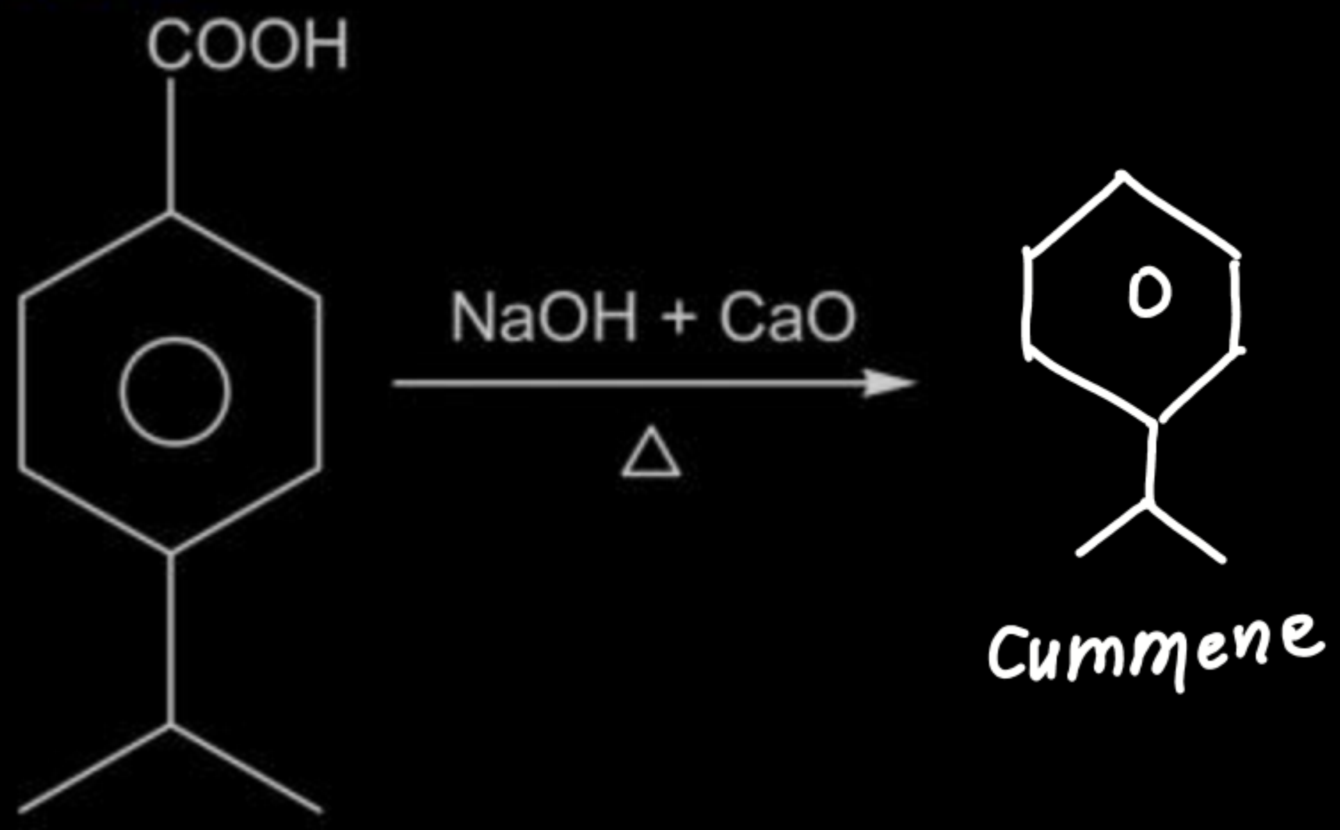
Ques.



Ques.

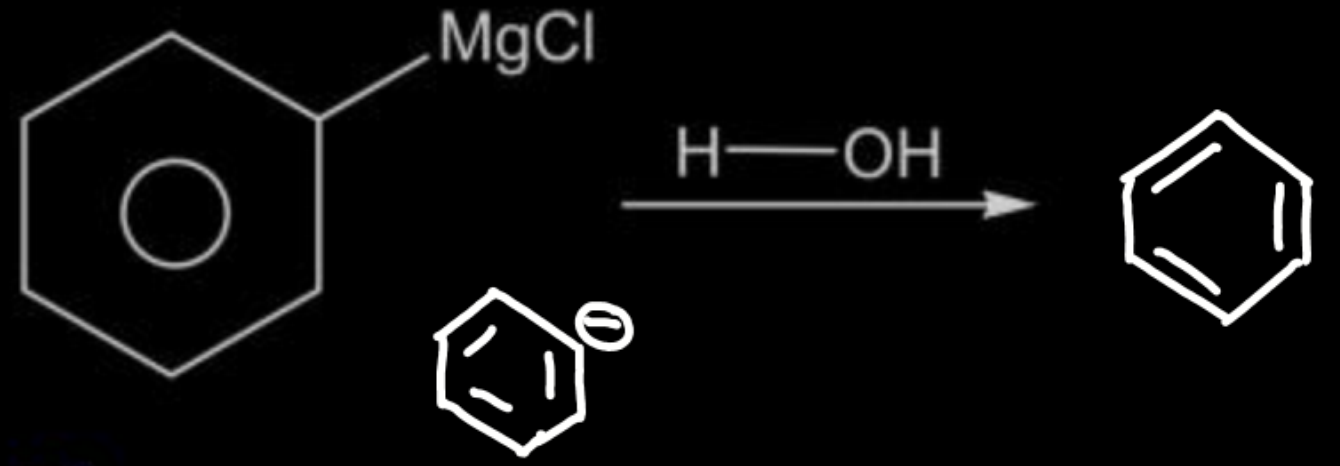


Ques.

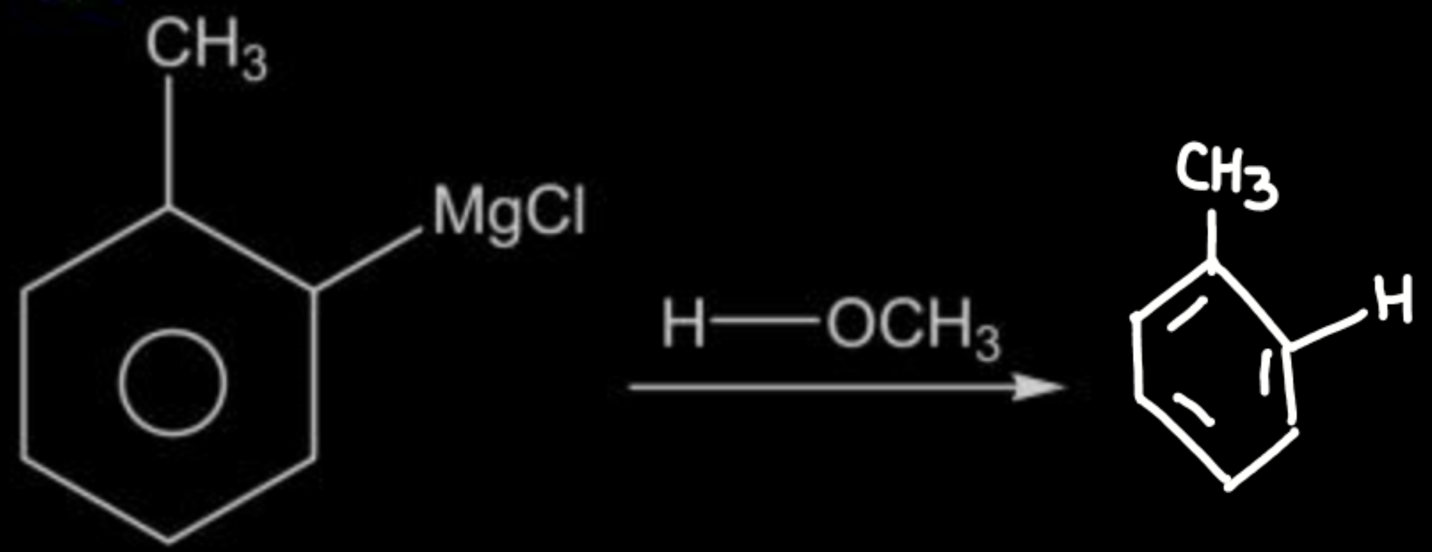


(VII) From Grignard Reagent:

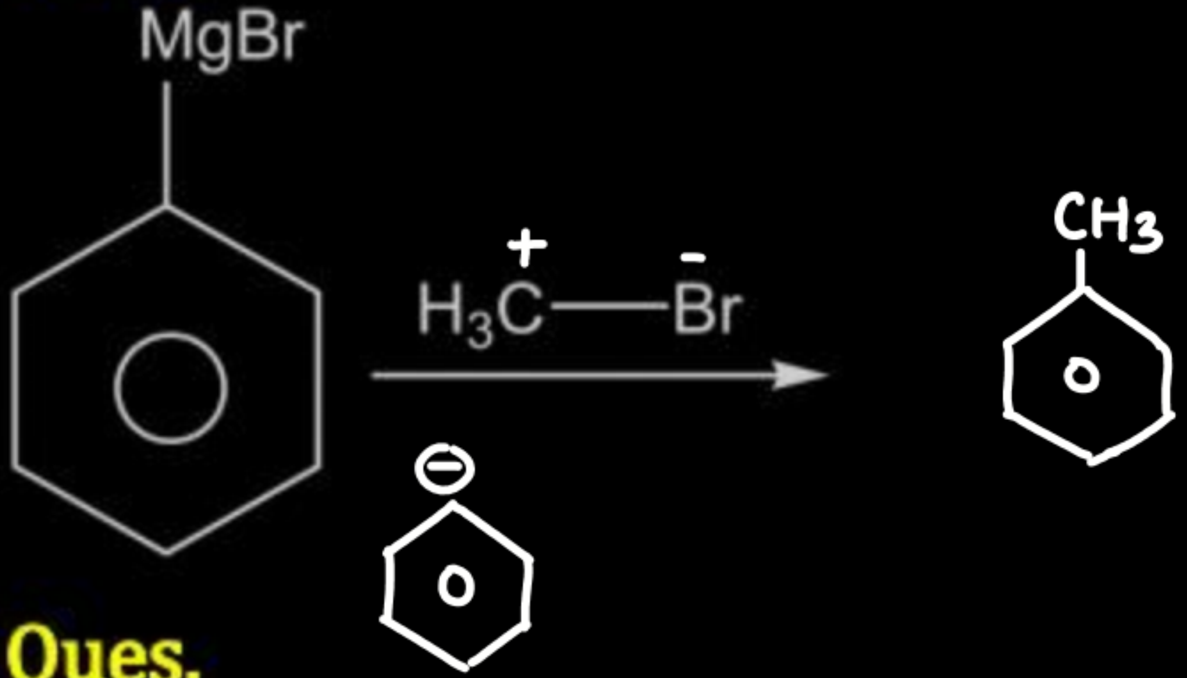
Ques.



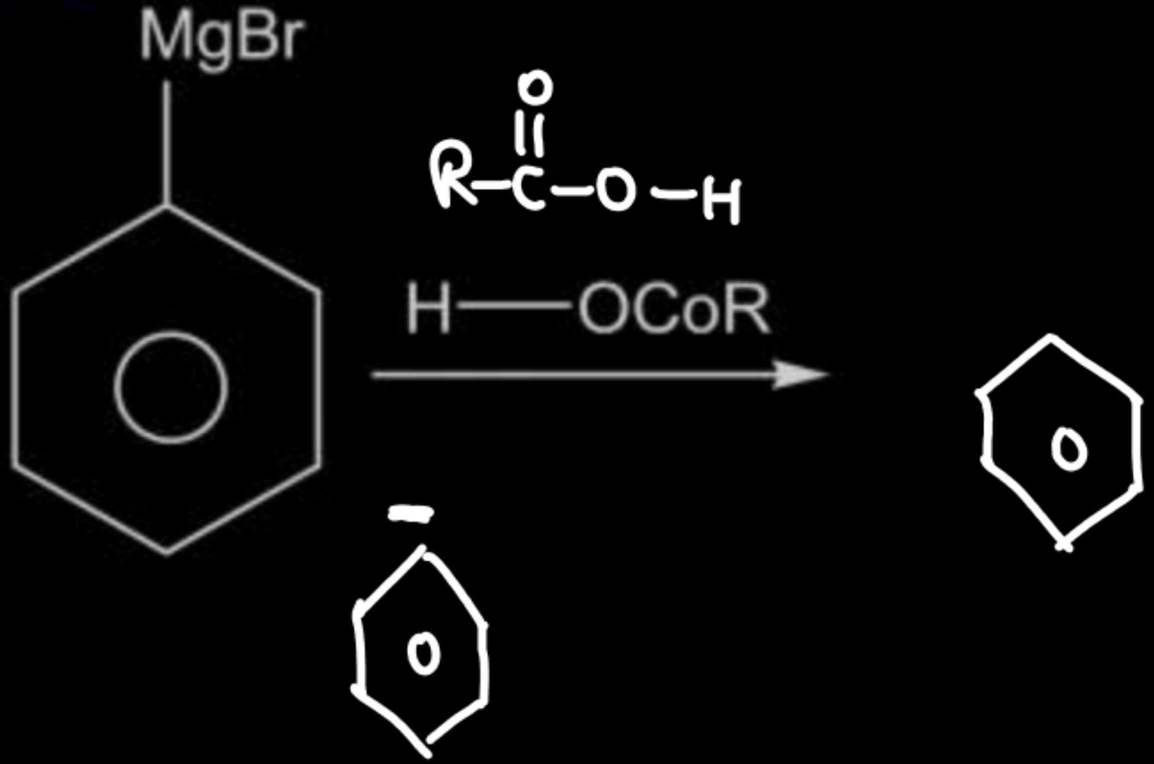
Ques.



Ques.

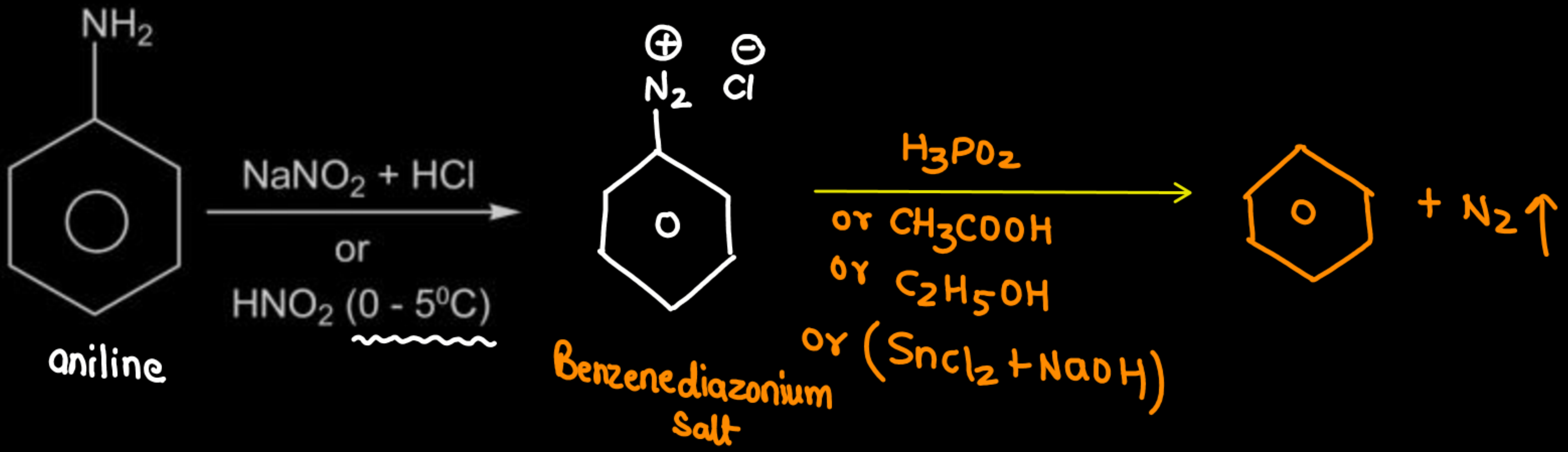


Ques.

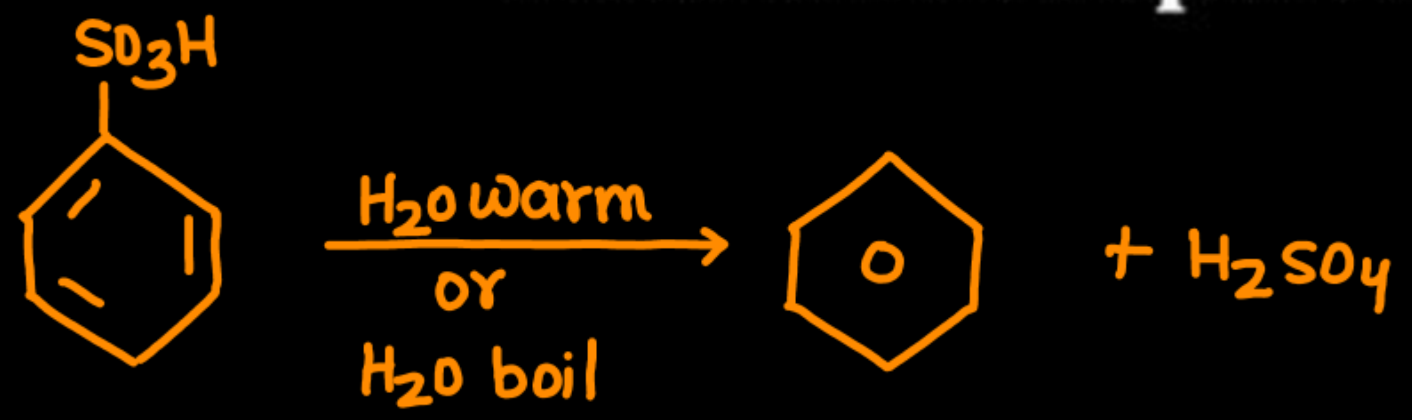


(VIII) From Diazonium Salt:

Ques.



Benzene Sulphonic Acid ⟶ Benzene



Chemical Reaction of Aromatic H.C

① Substitution Reaction

1. nitration $\xrightarrow[\text{Conc } H_2SO_4]{\text{Conc } HNO_3}$ NO_2^+
2. nitrosylation $\xrightarrow{NaNO_2/HCl}$ NO^+
3. Sulphonation $\xrightarrow[\text{or Fuming } H_2SO_4]{H_2S_2O_7}$ $\oplus SO_3H$
4. Halogenation $\xrightarrow[\text{Lewis Acid } FeX_3/AlX_3]{X_2}$ $X^{\oplus}$
5. Friedal craft alkylation $\longrightarrow$ $R-Cl + \text{anhy } AlCl_3 \rightarrow R^+ \rightarrow$ Carbocation Form & Rearrange
6. Friedal craft acylation $\longrightarrow$ $R-\overset{O}{\overset{||}{C}}-Cl + \text{anhy } AlCl_3 \rightarrow R-\overset{O}{\overset{||}{C}}{}^{\oplus}$

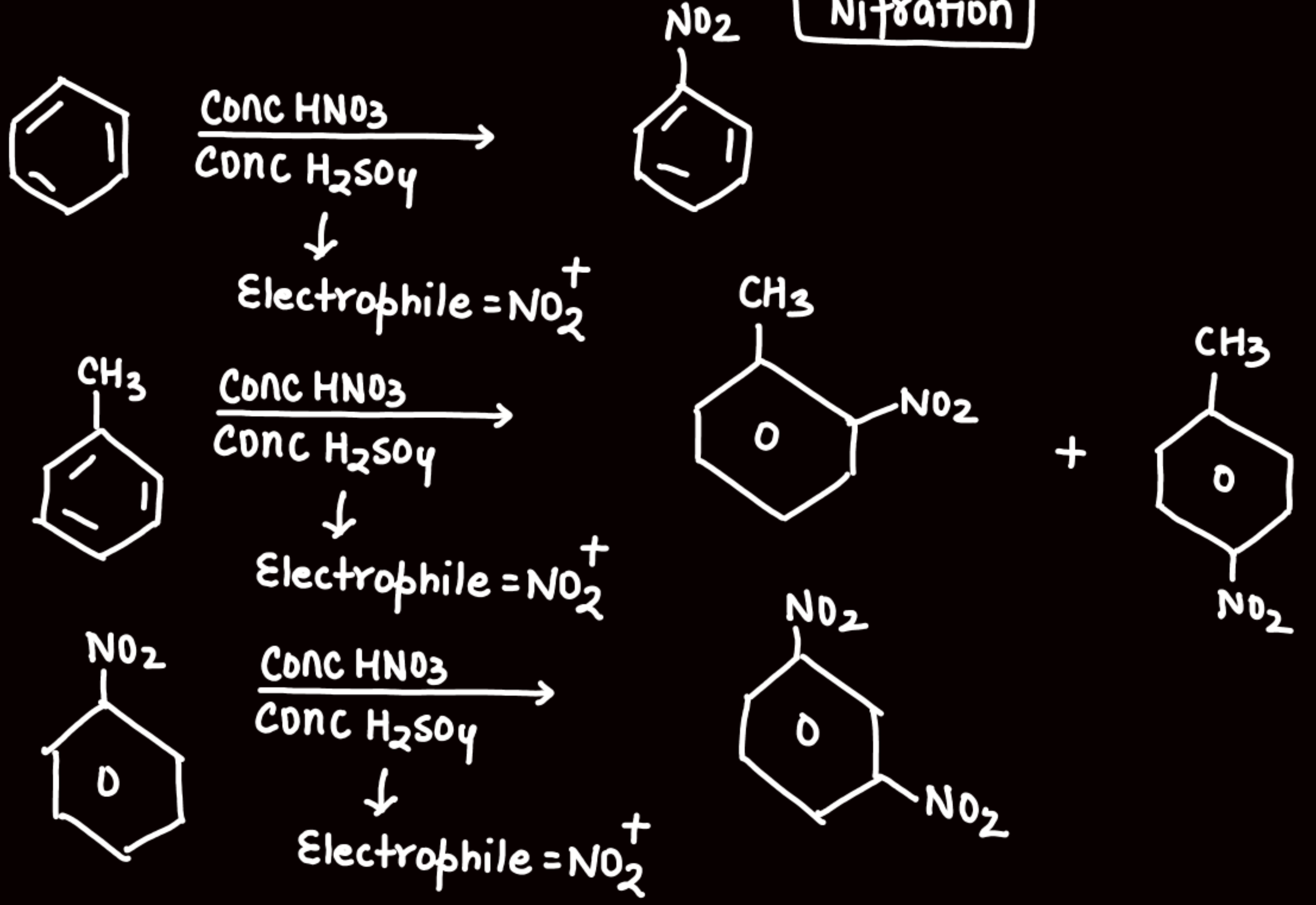
Addition Reaction

1. addition of H_2
2. addition of X_2
3. addition of O_3

Oxidation Reaction

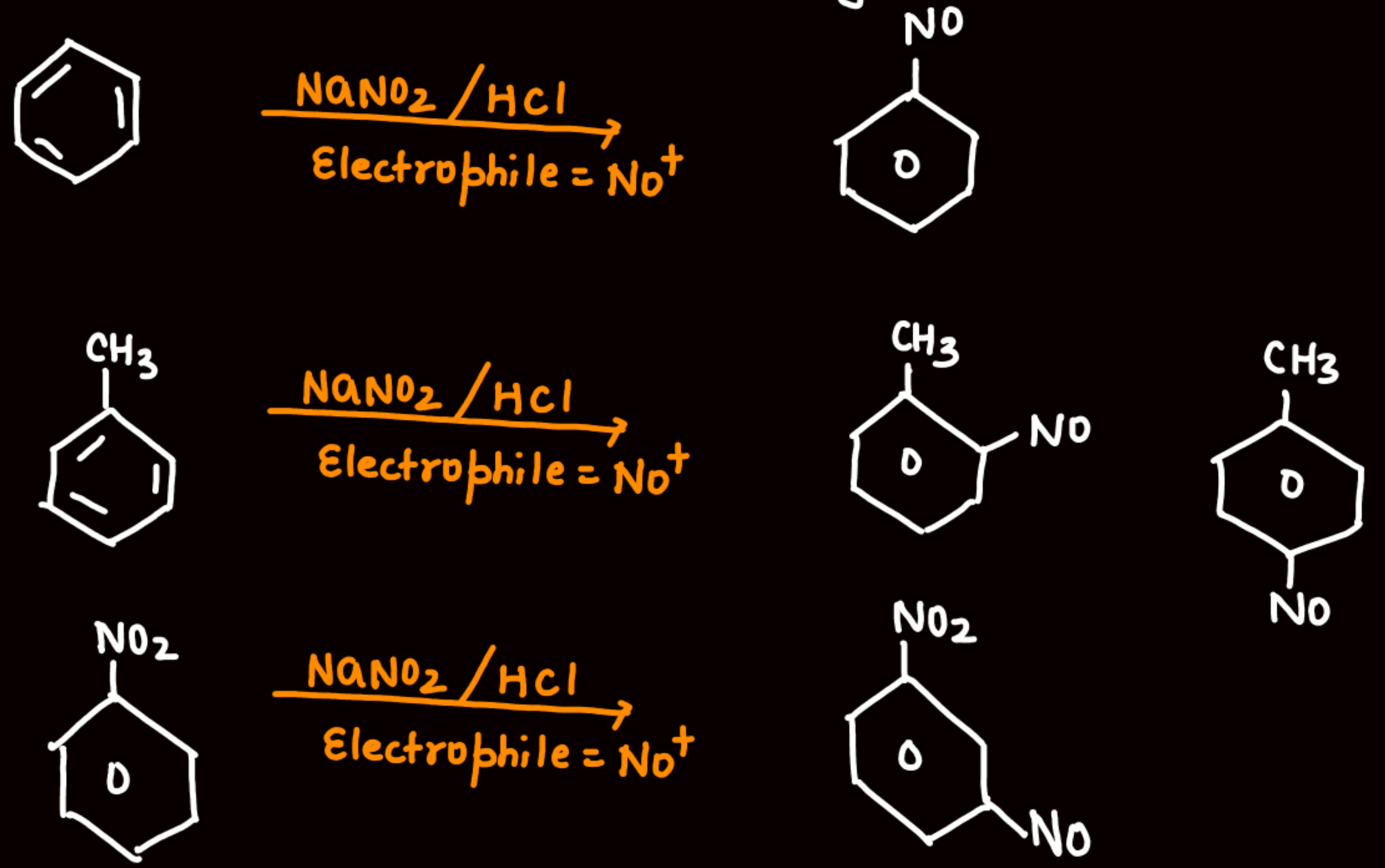
1. Catalytic oxidation
2. Sidechain oxidation

Nitration

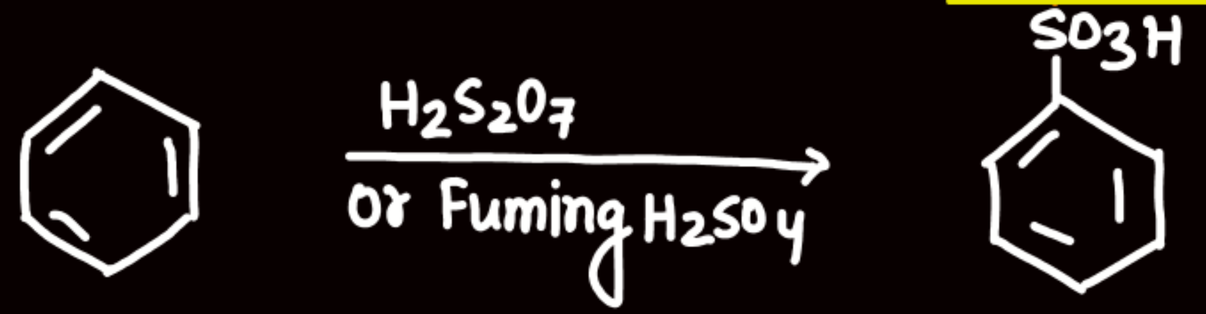


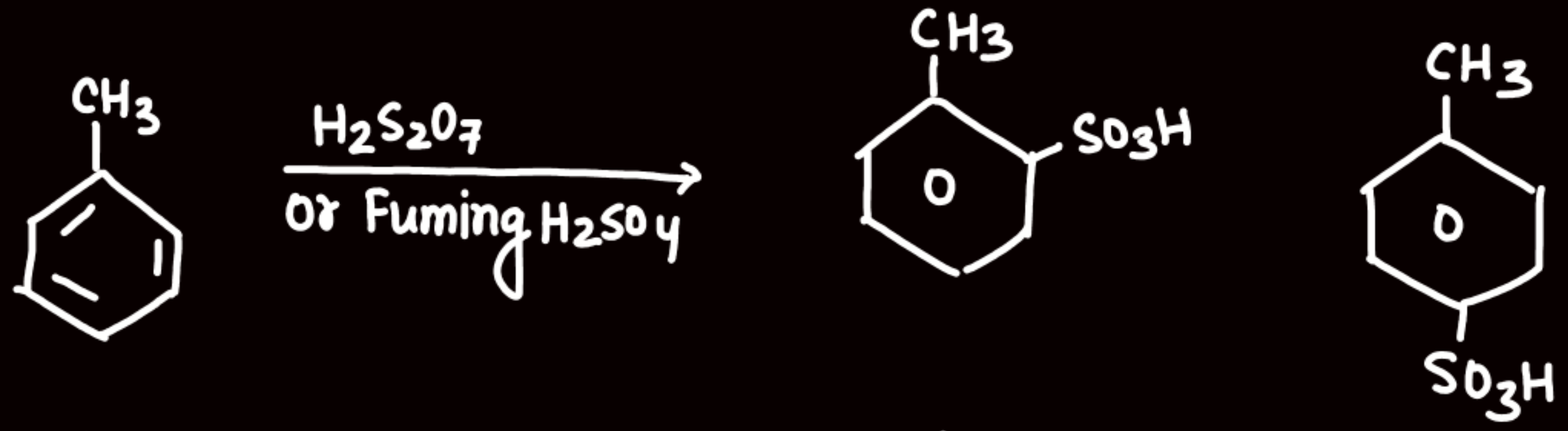
NO_2
Conc HNO_3
Conc H_2SO_4
Electrophile = NO_2^+
CH_3
Conc HNO_3
Conc H_2SO_4
Electrophile = NO_2^+
CH_3
NO_2
+
CH_3
NO_2
NO_2
Conc HNO_3
Conc H_2SO_4
Electrophile = NO_2^+
NO_2
NO_2

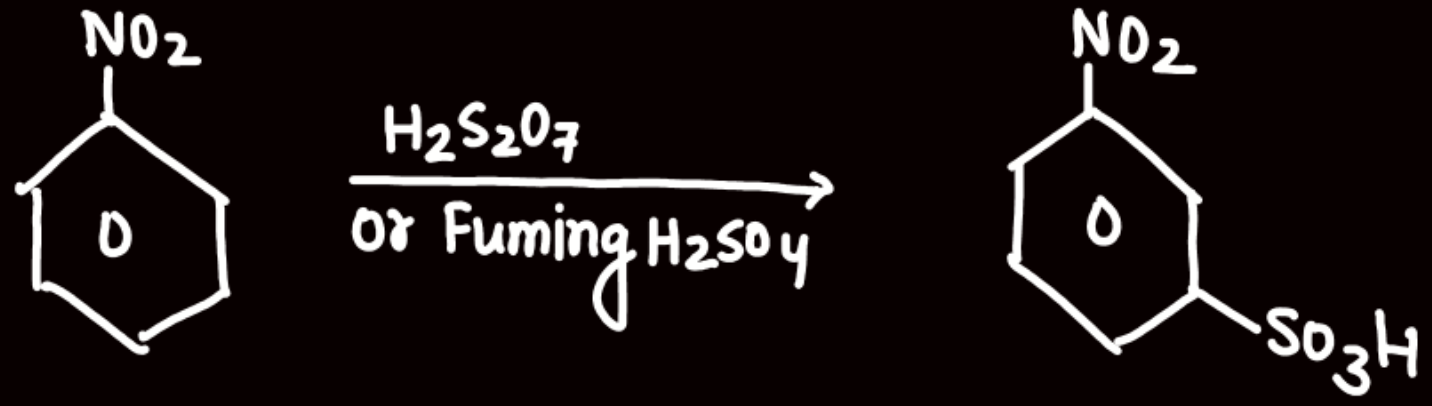
nitrosylation



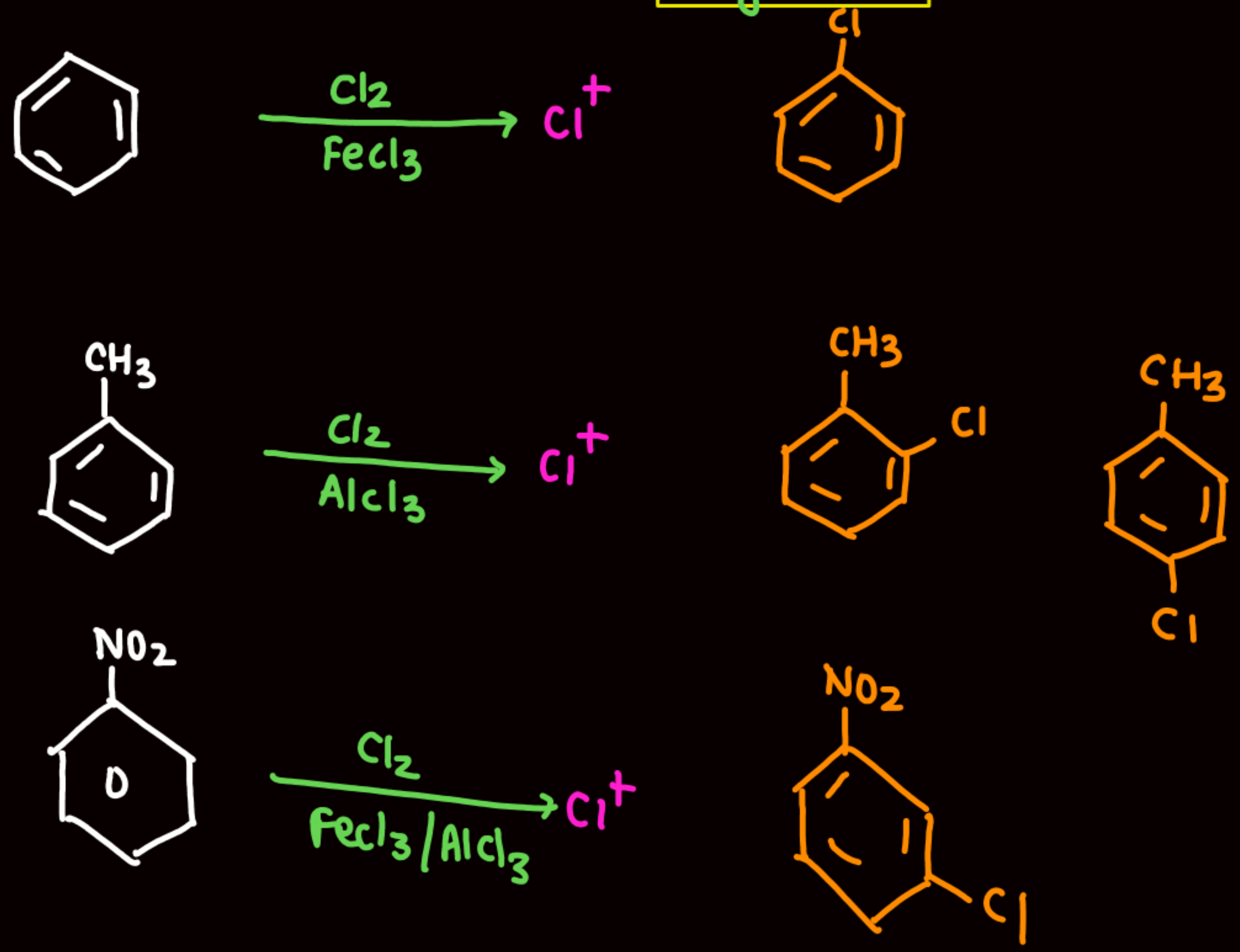
Sulphonation



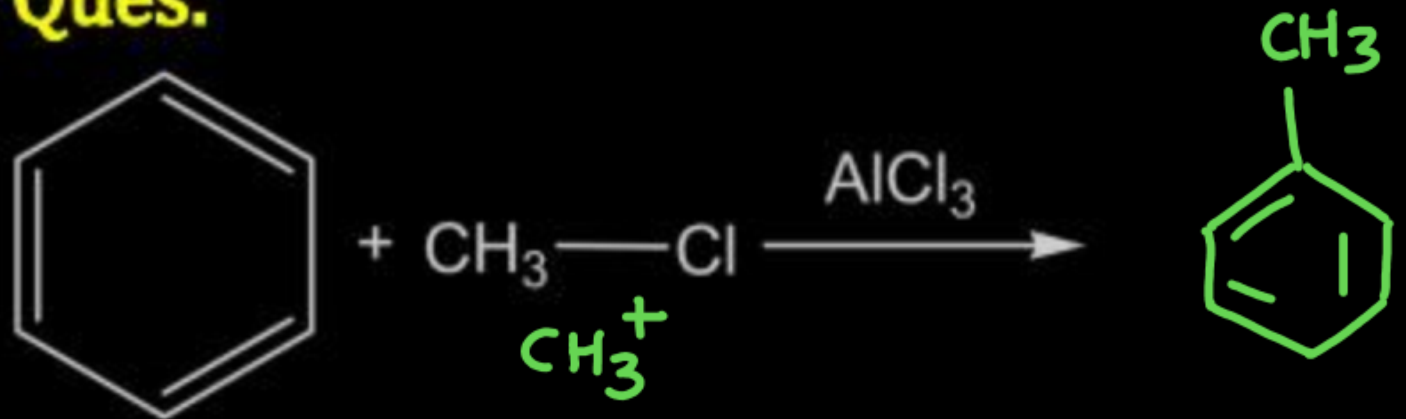




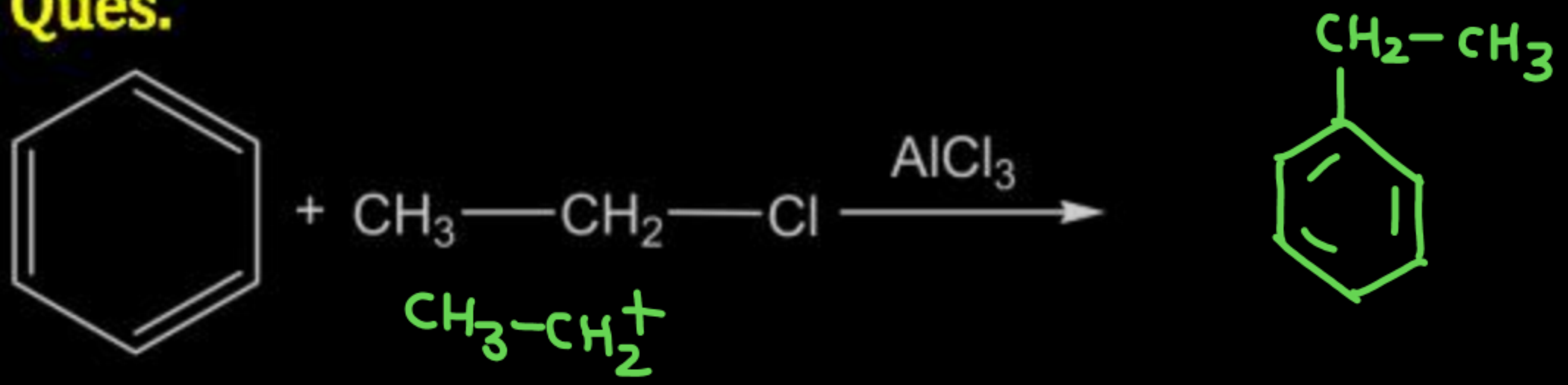
Halogenation



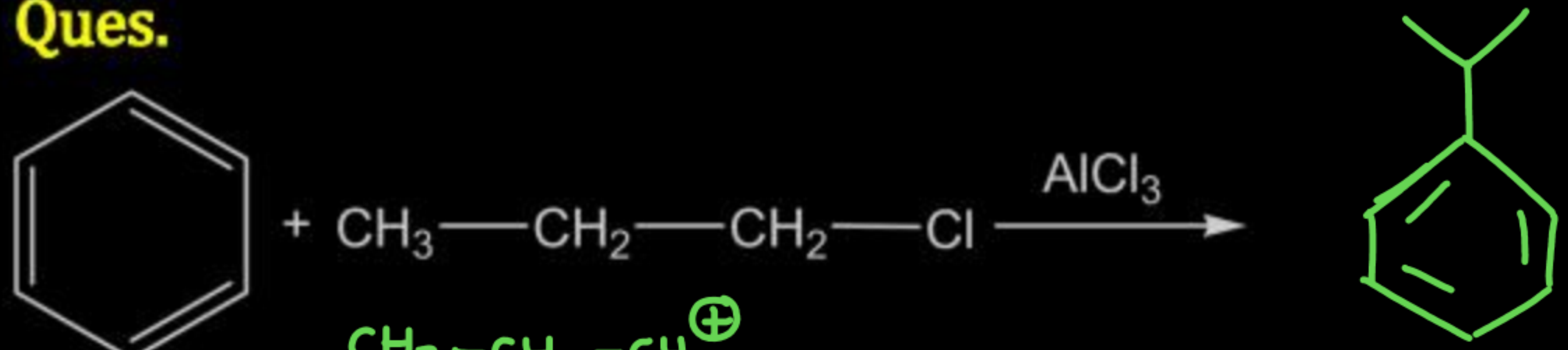
Ques.



Ques.



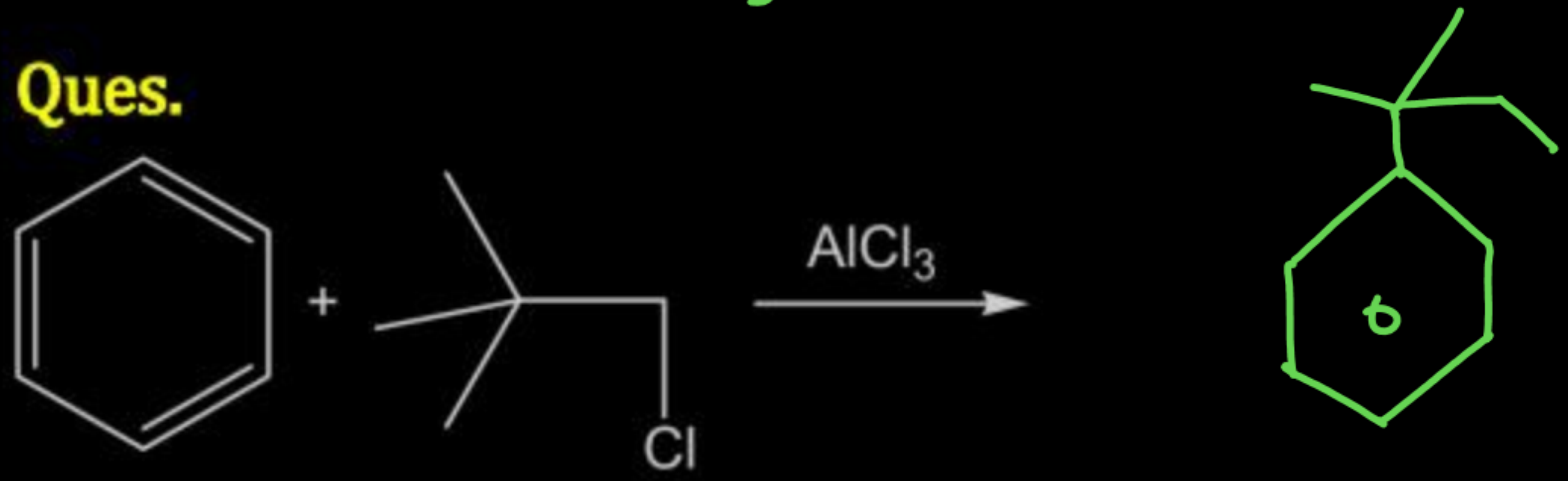
Ques.



$CH_3-CH_2-CH_2^{\oplus}$

$CH_3-\overset{\oplus}{C}H-CH_3$

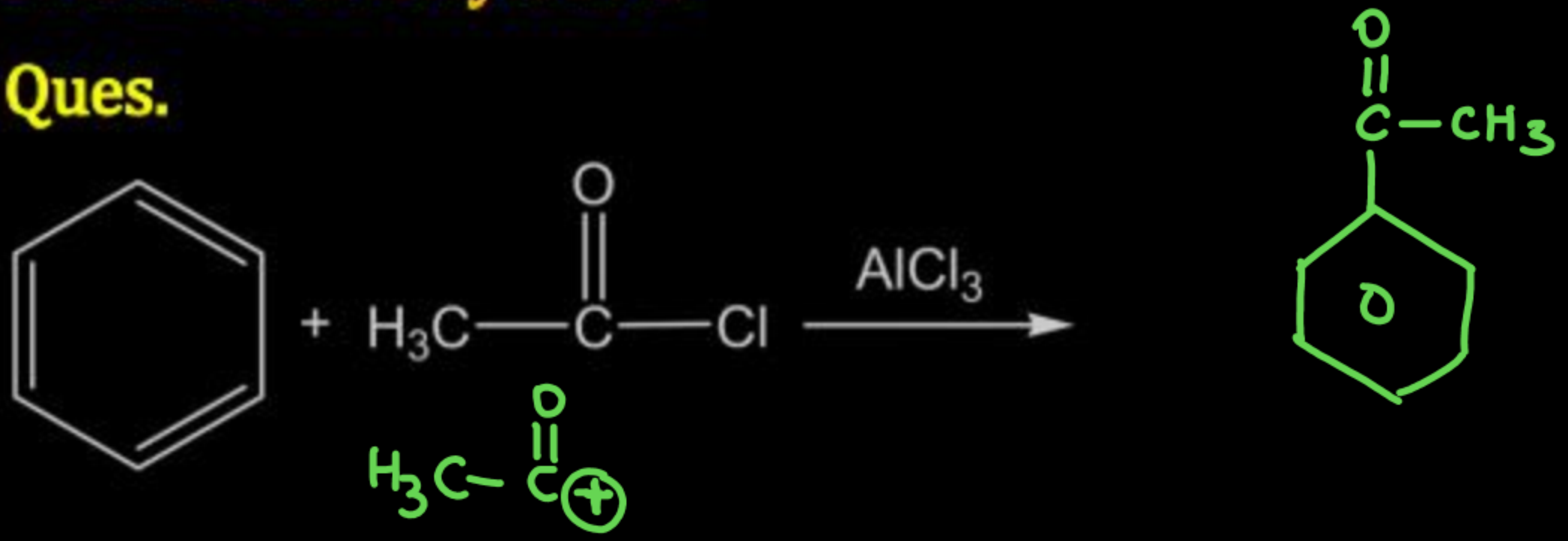
Ques.



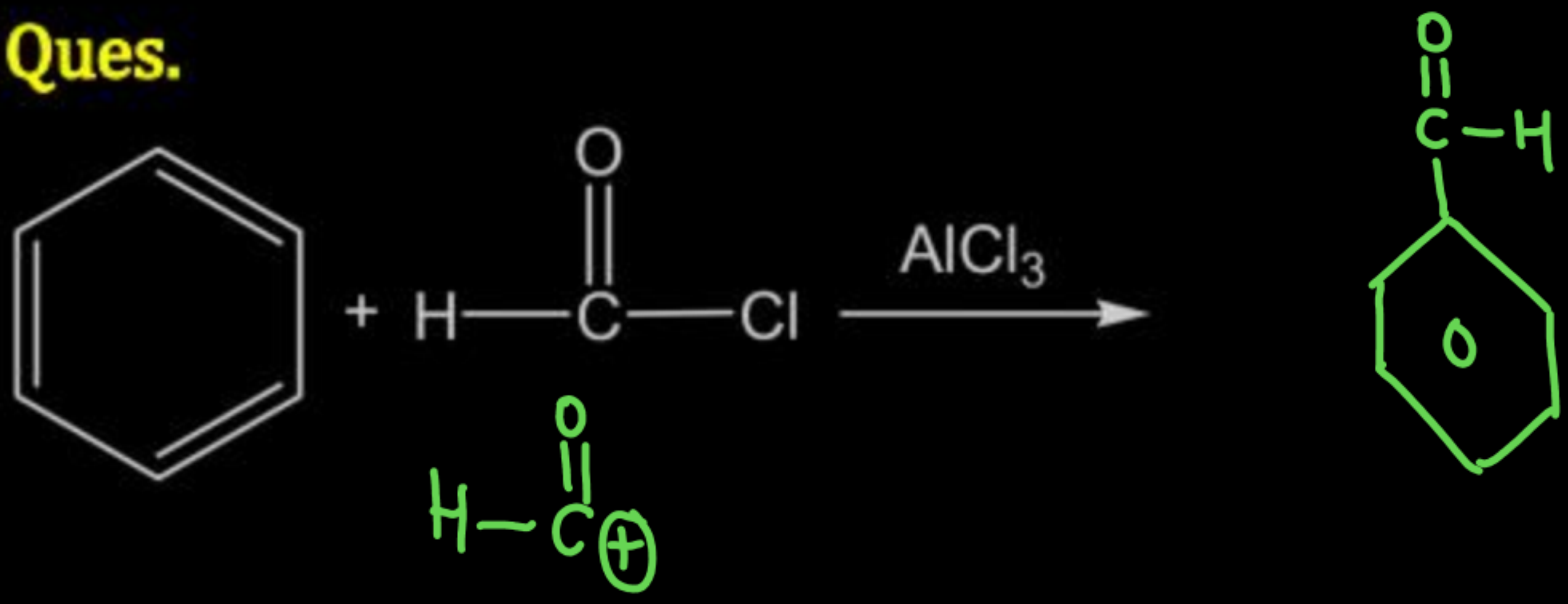


Friedal Craft Acylation:

Ques.



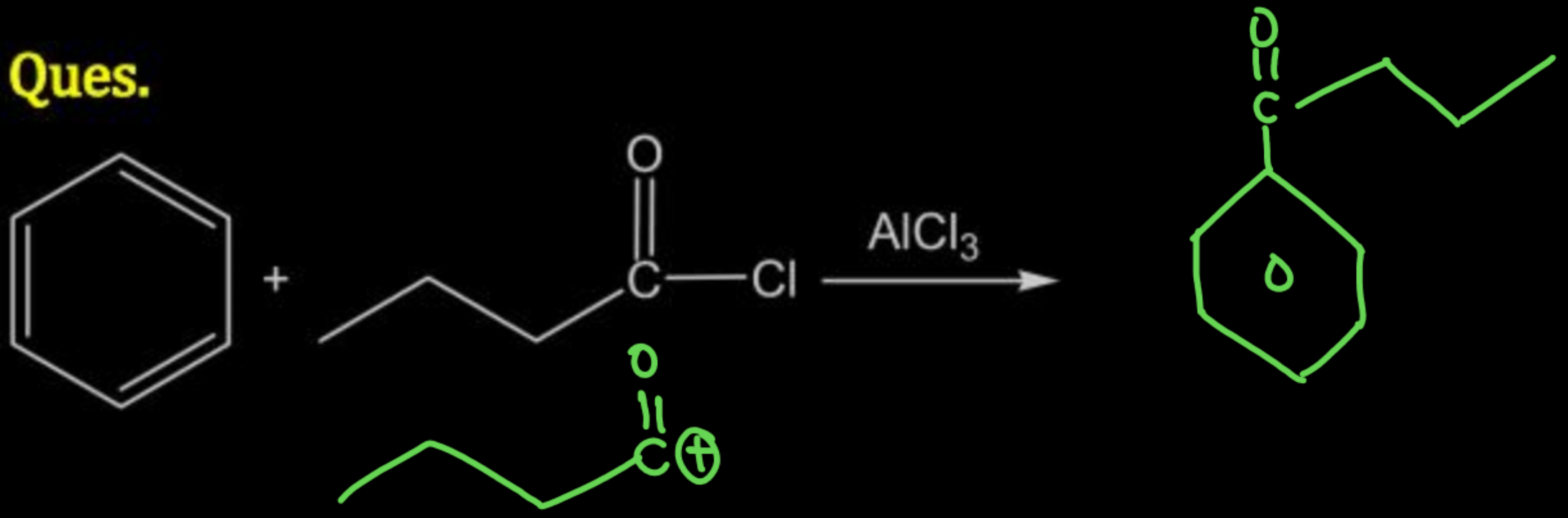
Ques.



Ques.



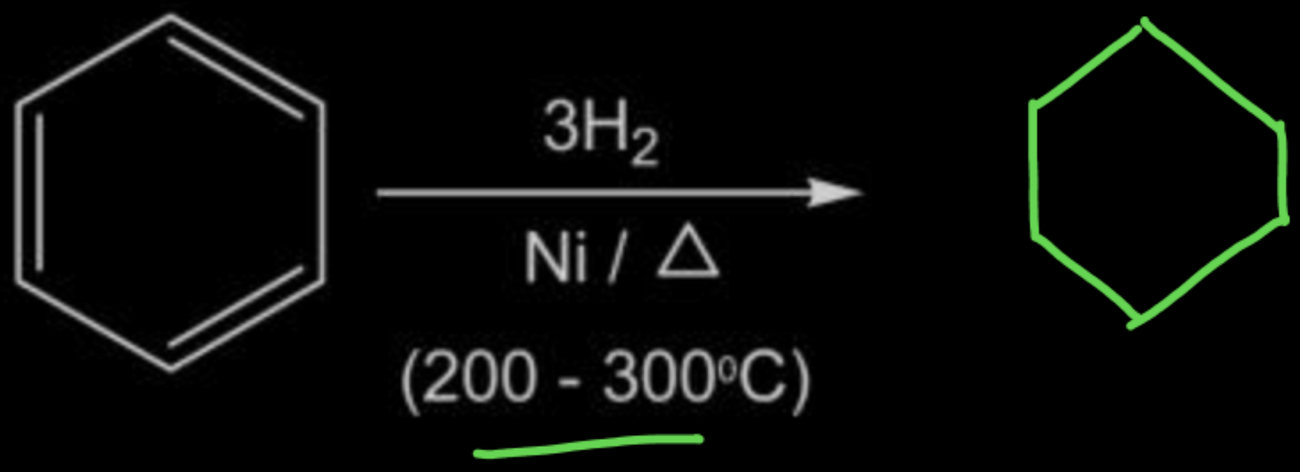
Ques.



Addition of H_2:

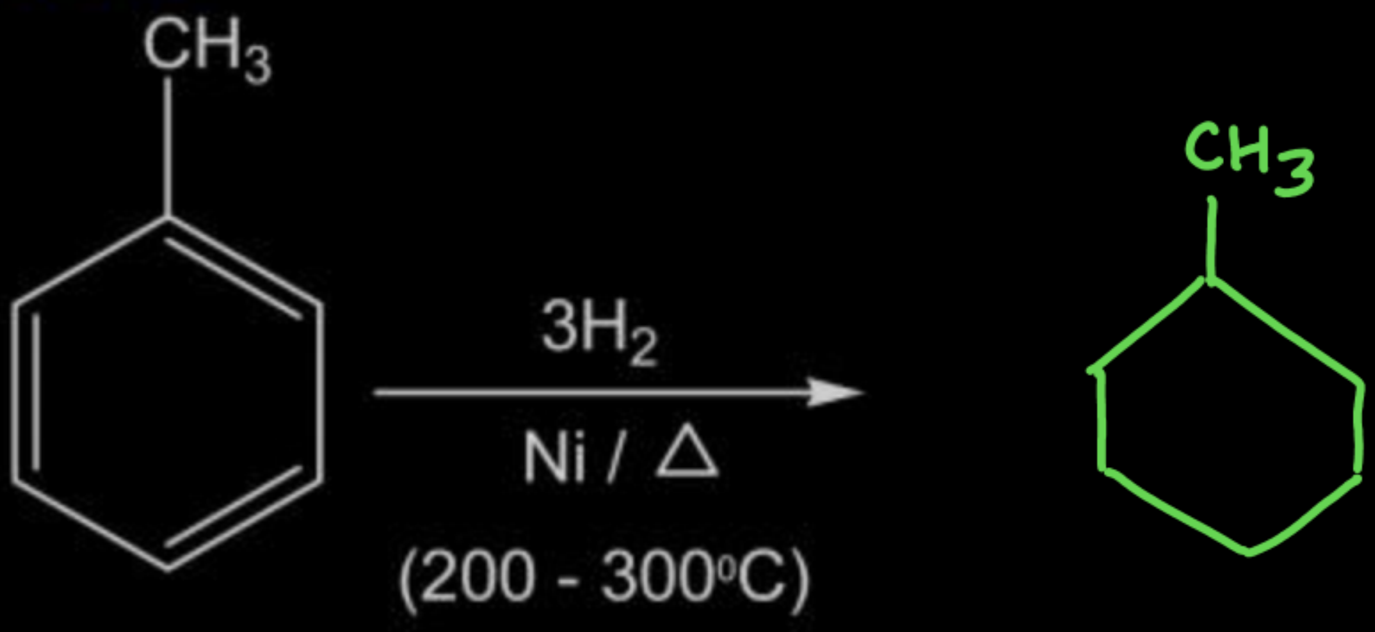
Complete Hydrogenation:

Ques.

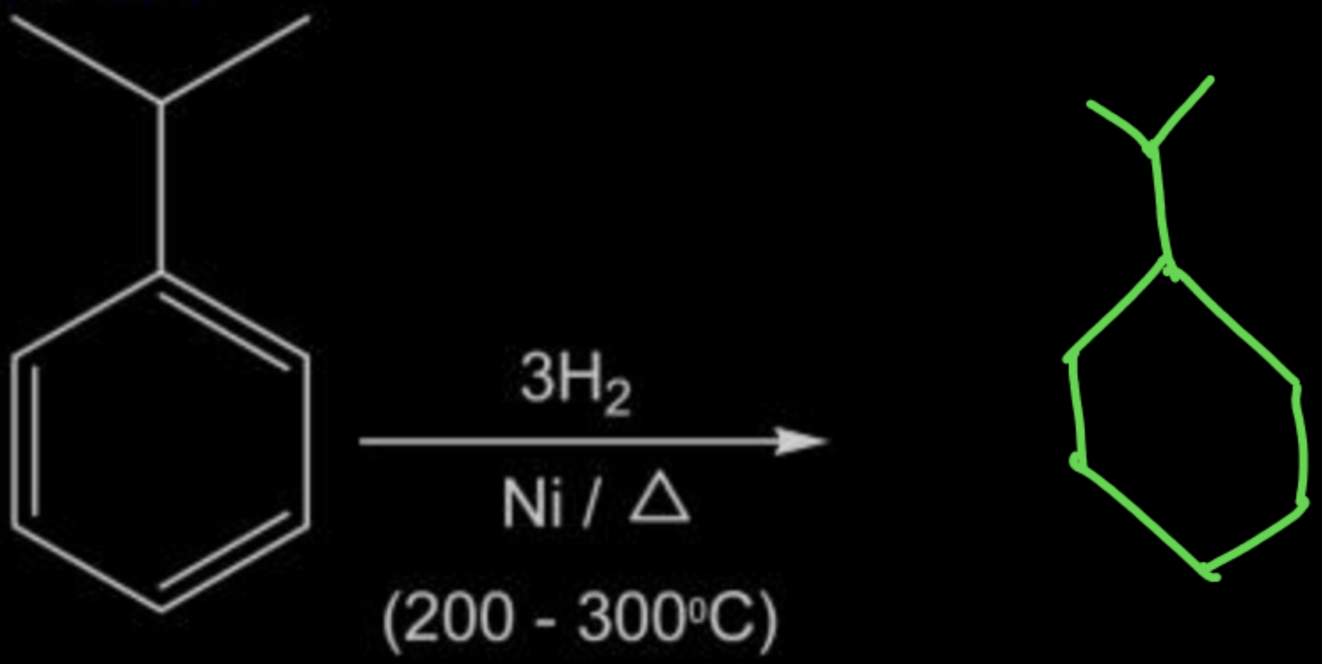


(This reaction is not possible at normal temp)

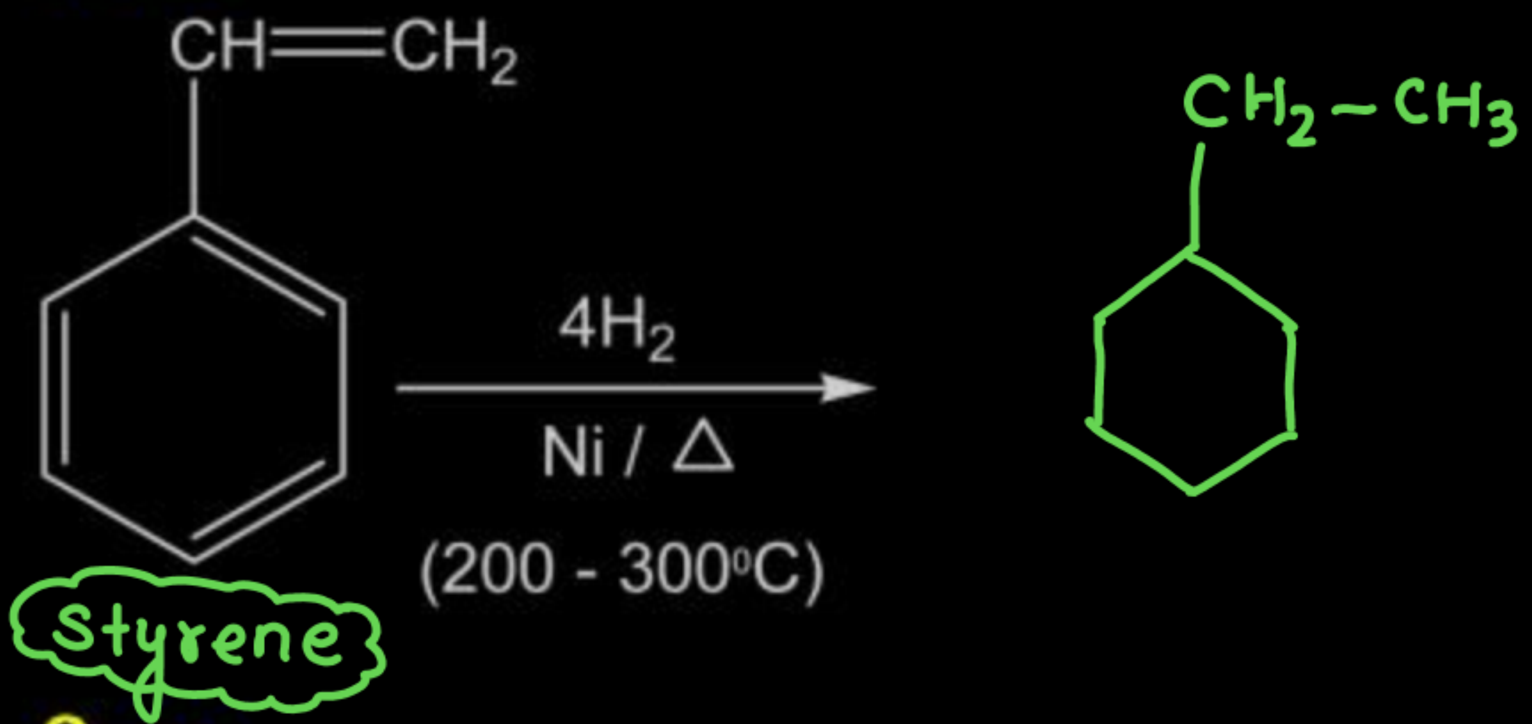
Ques.



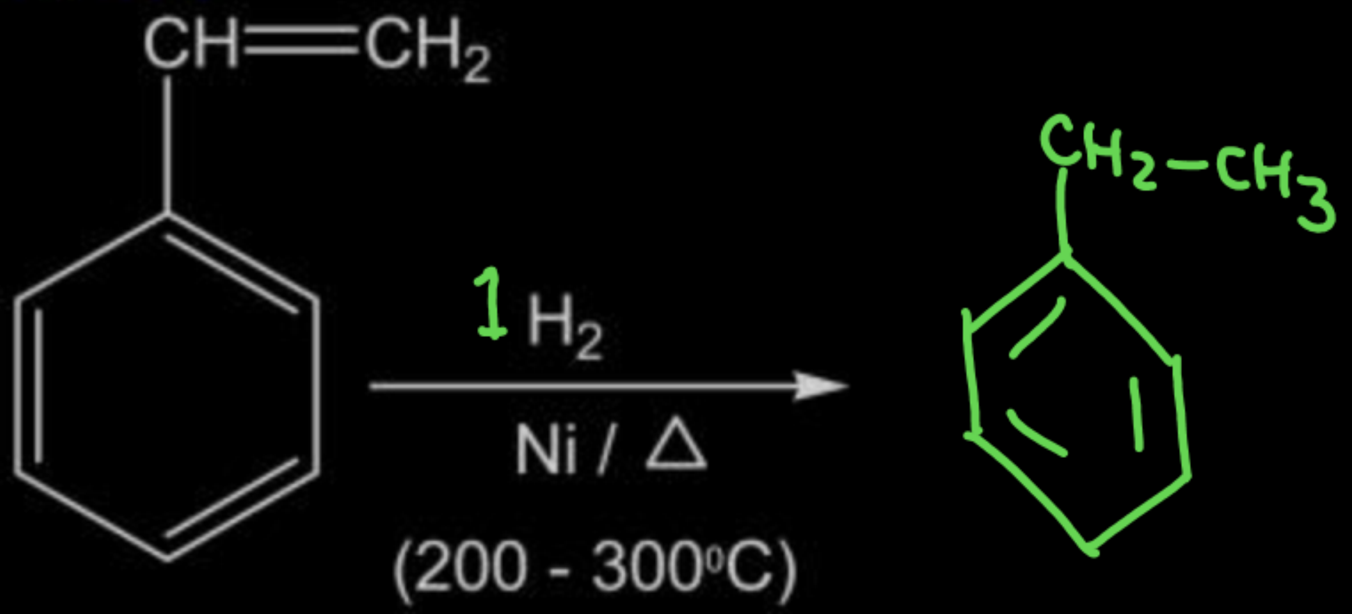
Ques.



Ques.

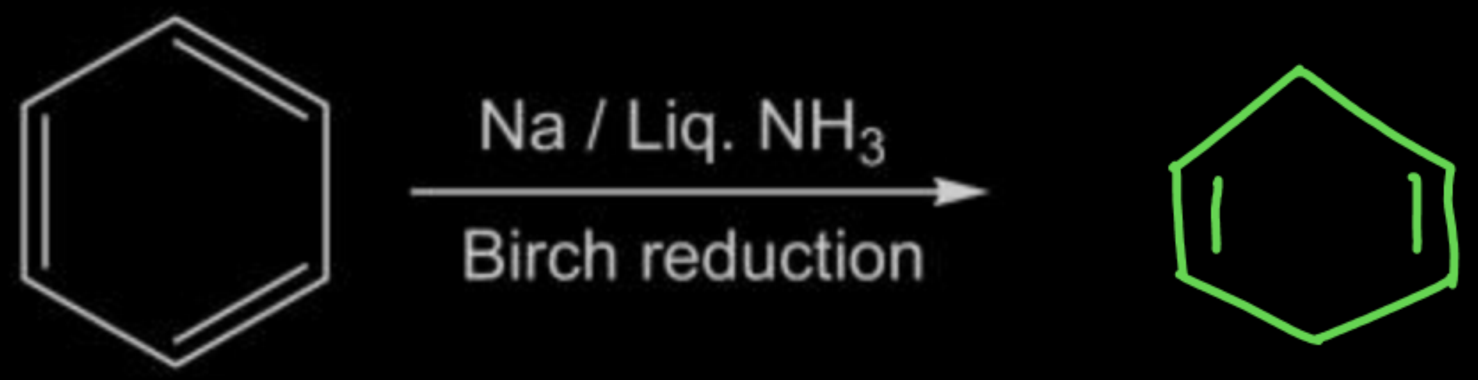

CH=CH2
4H2
Ni / Δ
(200 - 300°C)
CH2 – CH3
Styrene

Ques.


CH=CH2
1 H2
Ni / Δ
(200 - 300°C)
CH2 – CH3

Partial Hydrogenation:

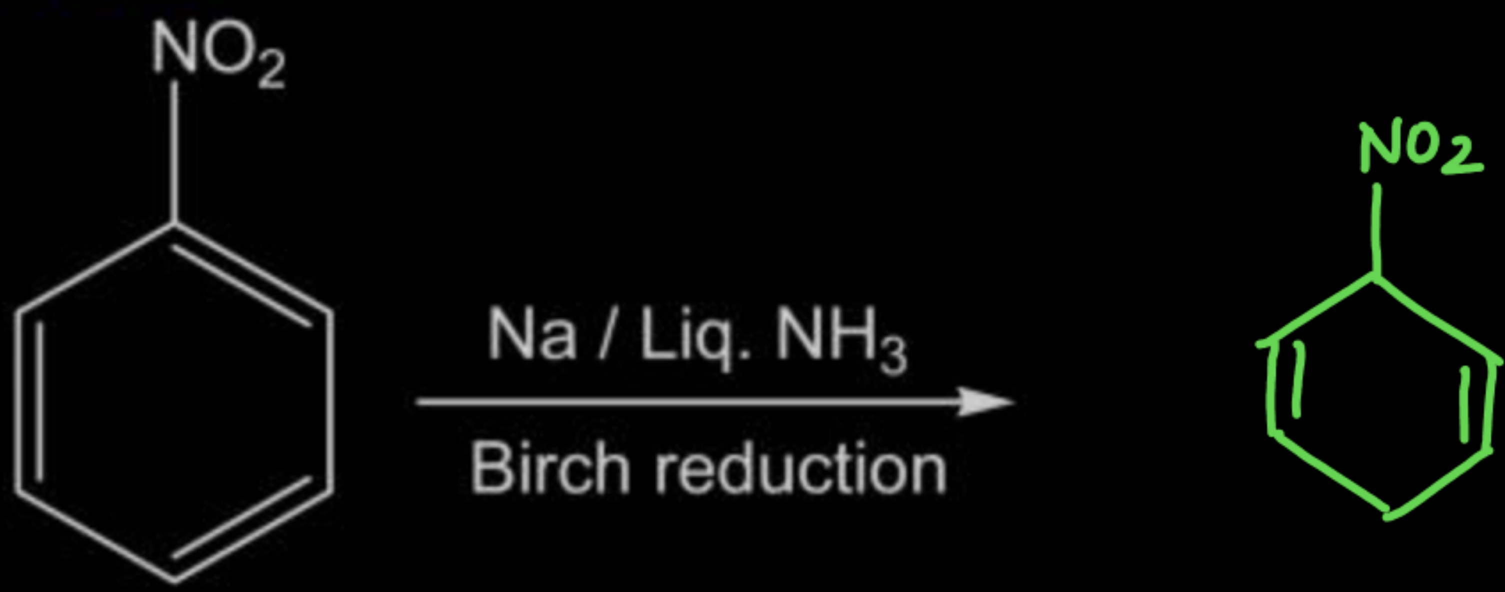
Ques.



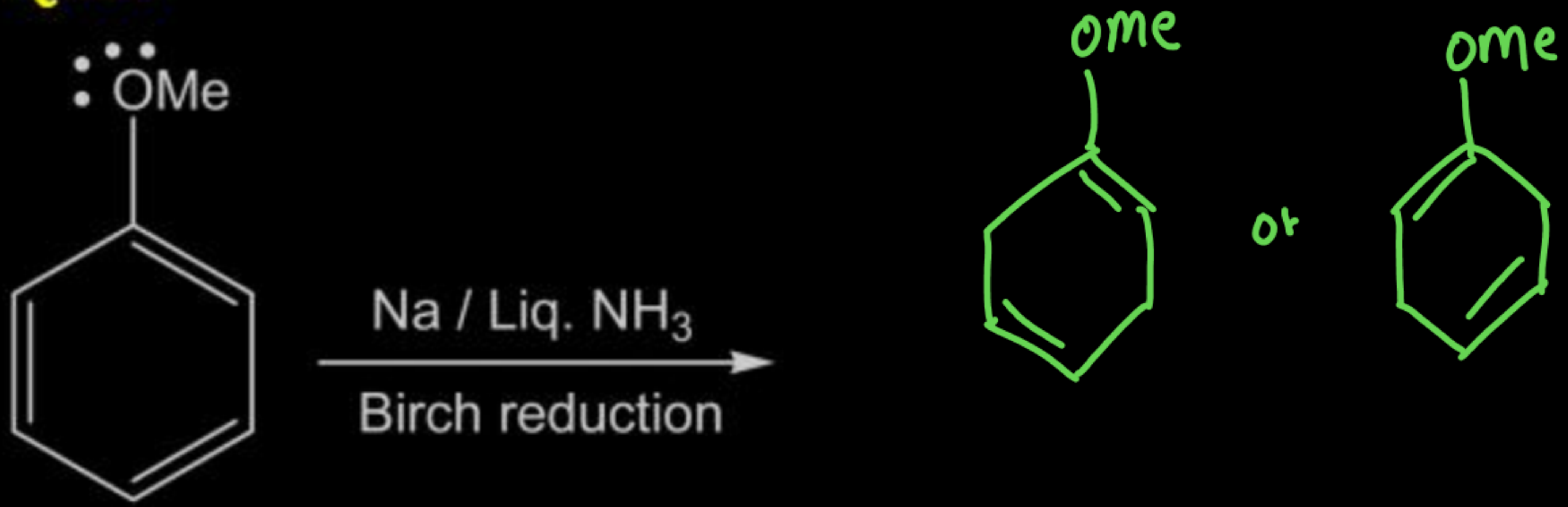
Ques.



Ques.

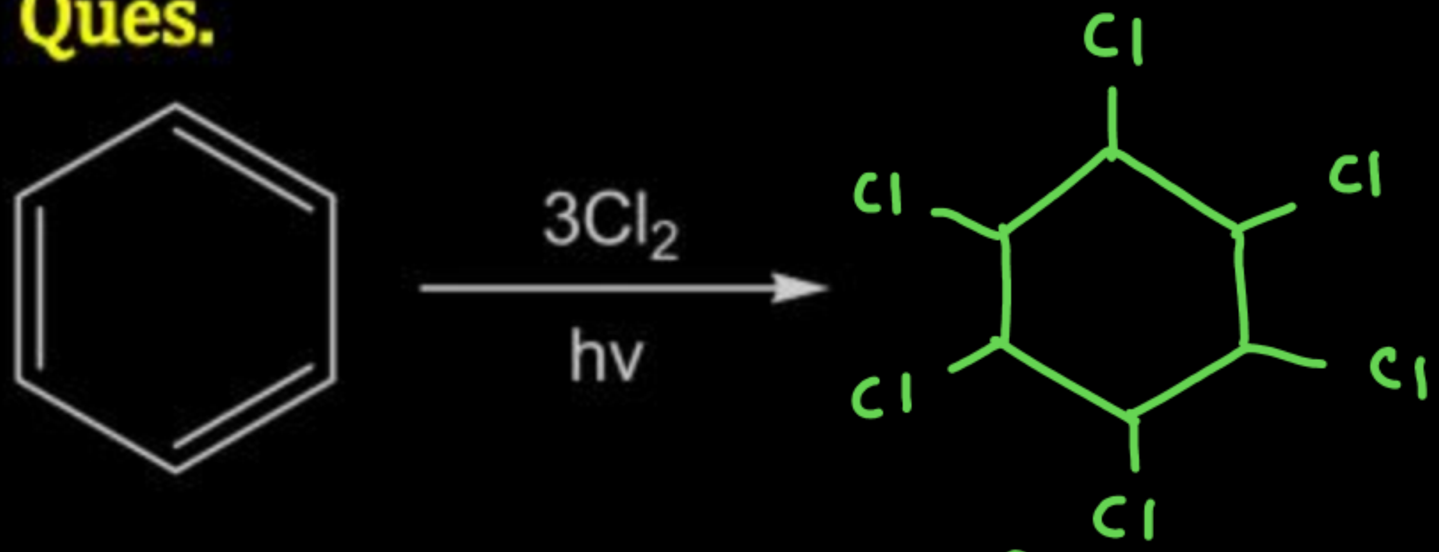

NO2
Na / Liq. NH3
Birch reduction
NO2

Ques.


OMe
Na / Liq. NH3
Birch reduction
ome
or
ome

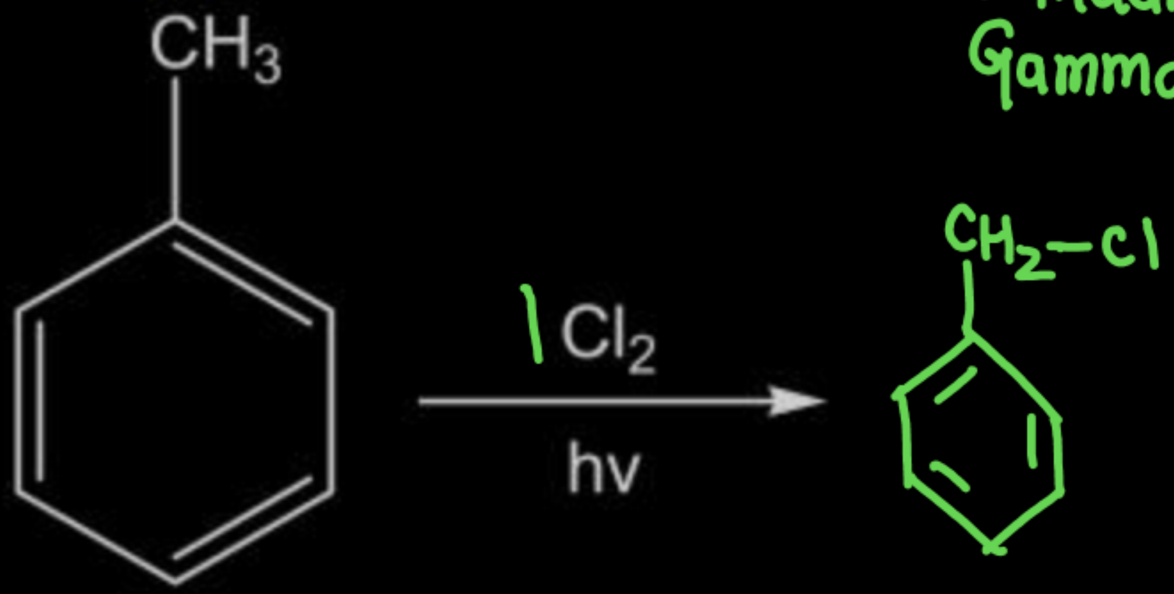
Addition of X_2:

Ques.

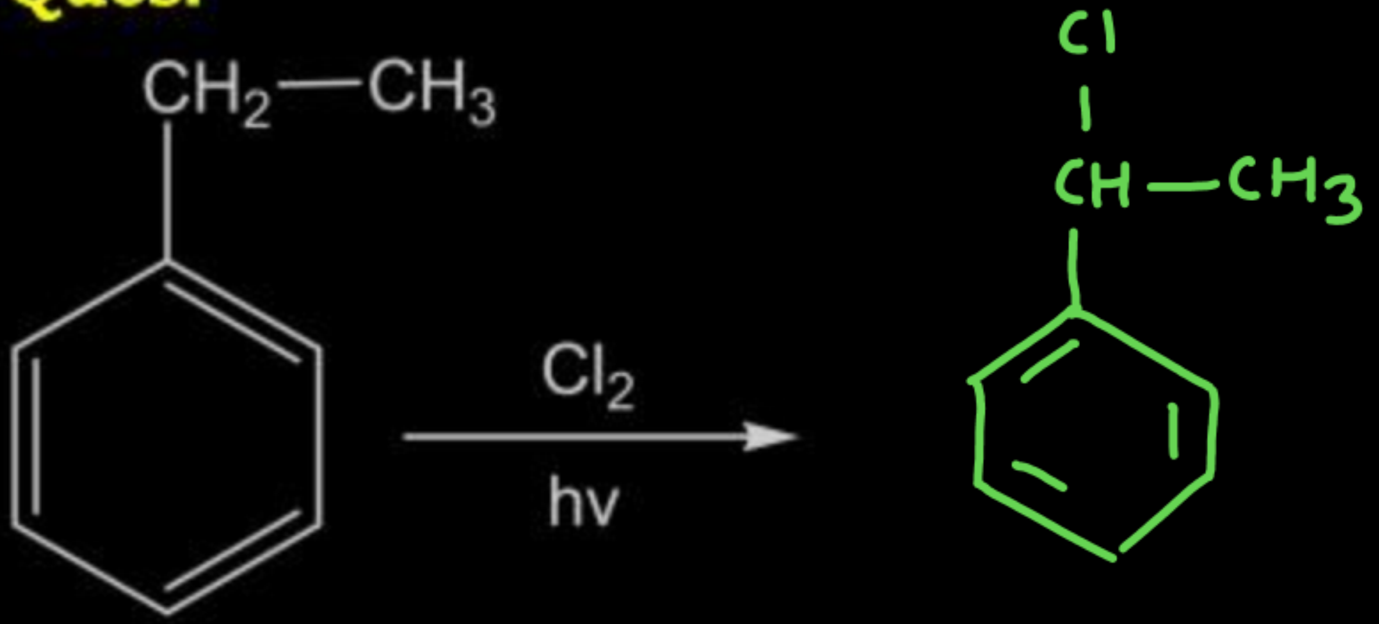


Benzene hexachloride (6,6,6)
BHC
lindane (Power insecticide)
Gammaxene

Ques.

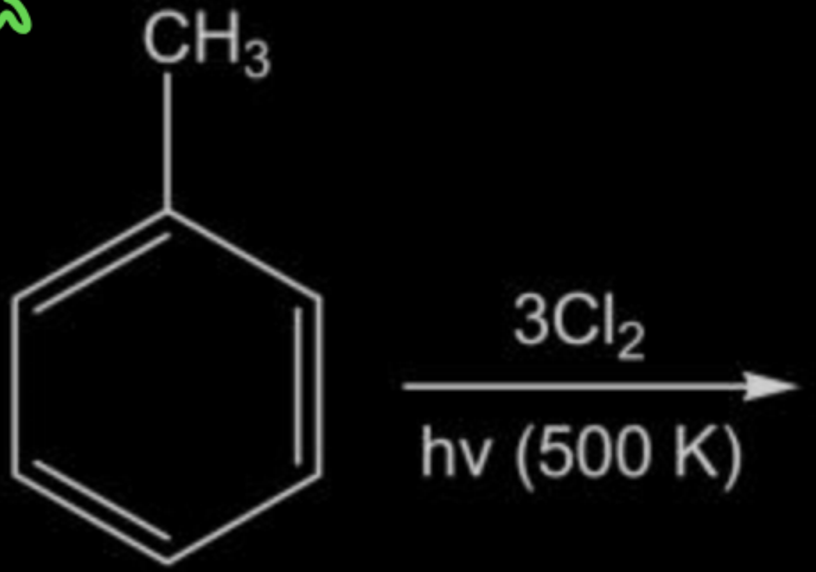


Ques.

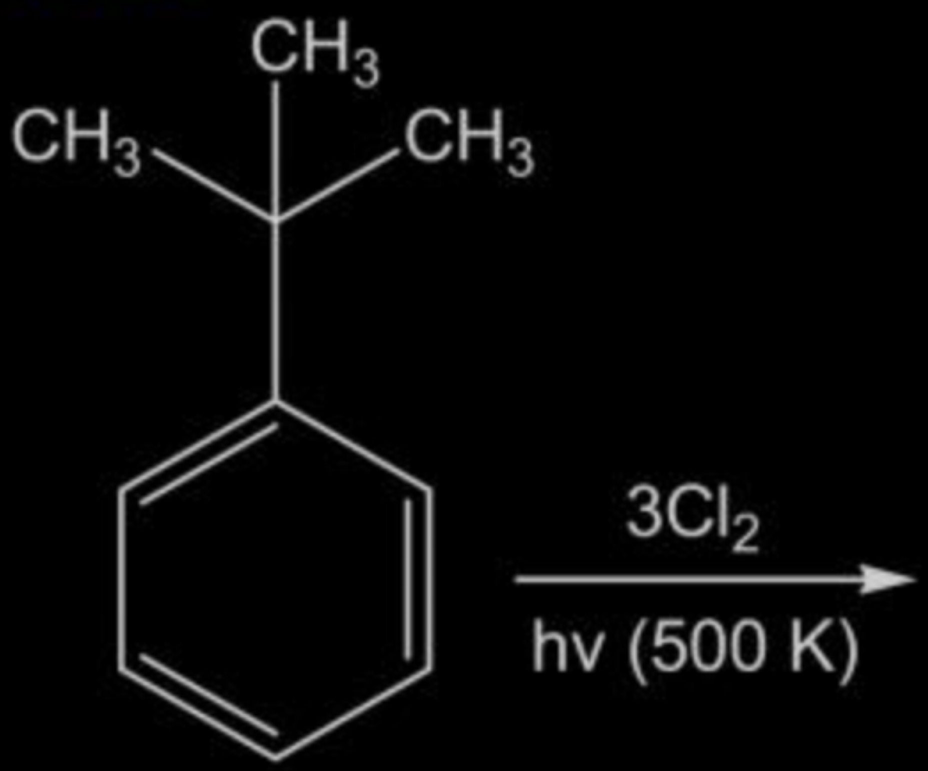


Ques.

HW

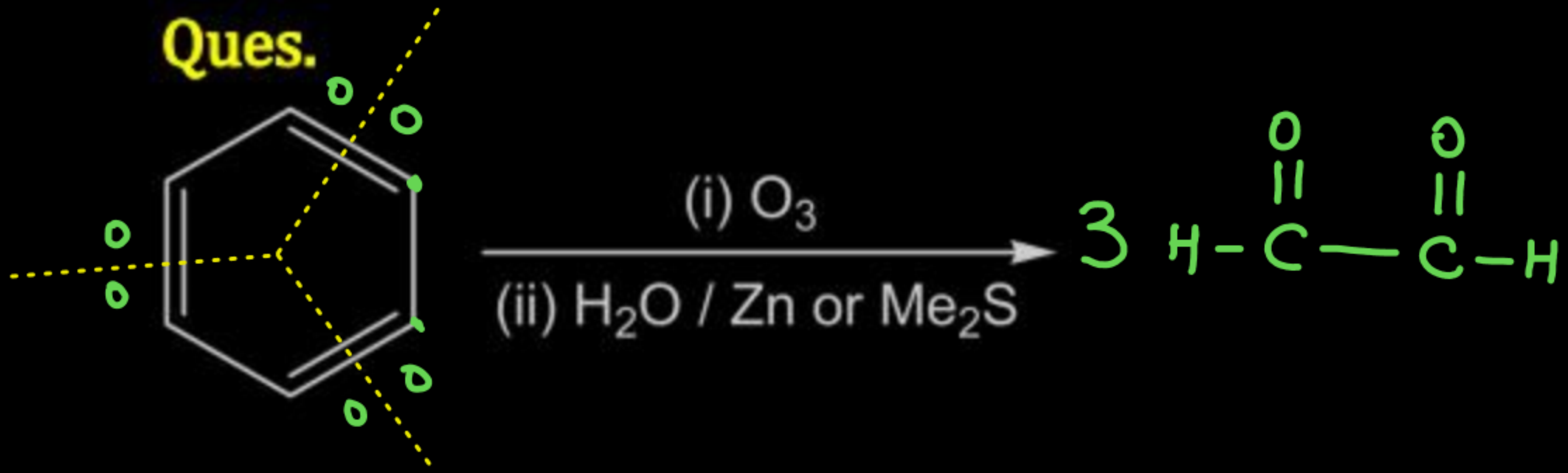


HW **Ques.**

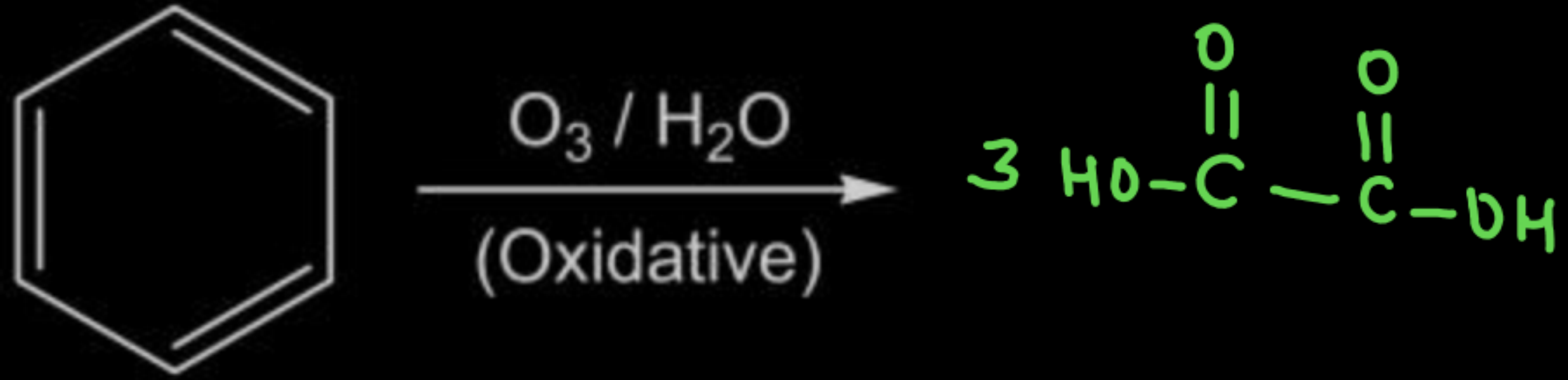


Addition of O_3:

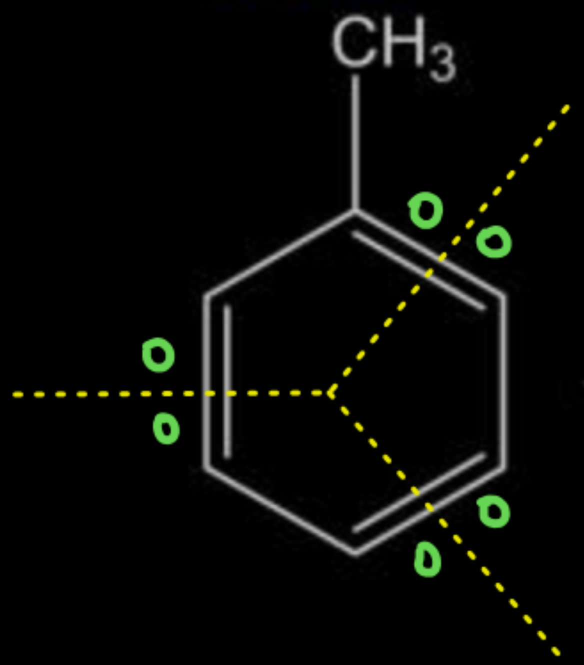
Ques.



Ques.

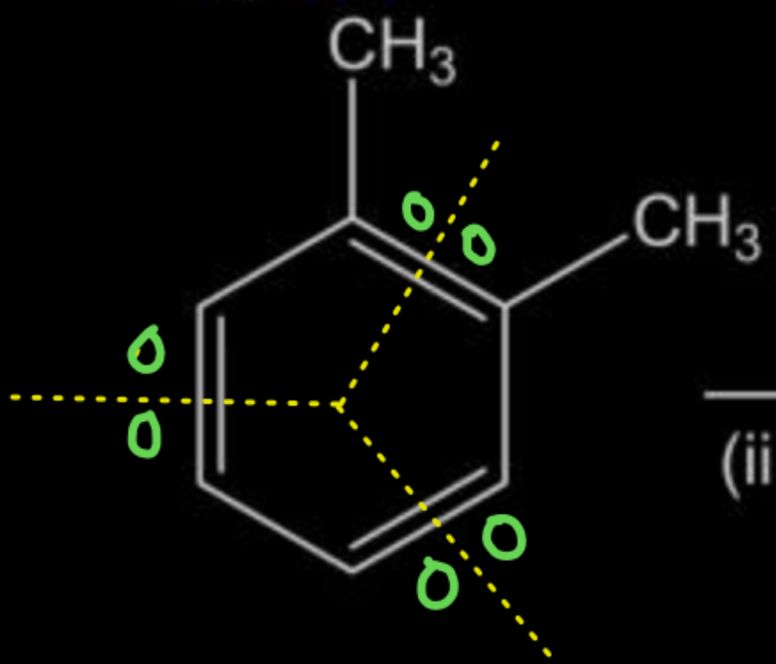


Ques.



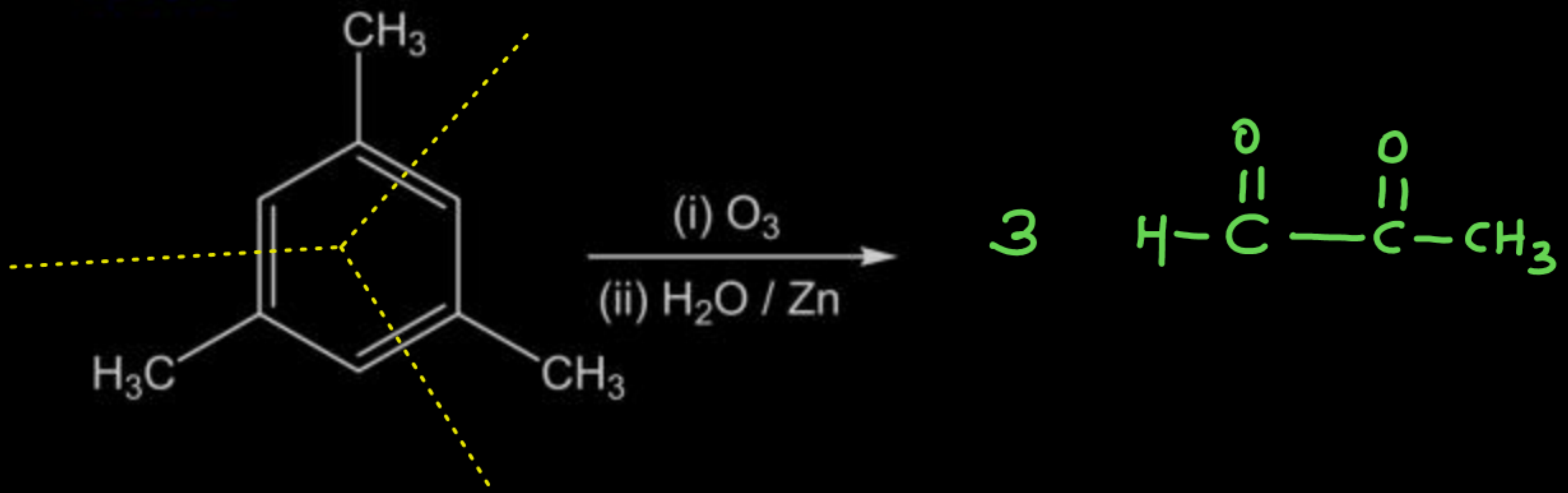
$$\xrightarrow[\text{(ii) } H_2O / Zn]{\text{(i) } O_3} 2\ H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

Ques.

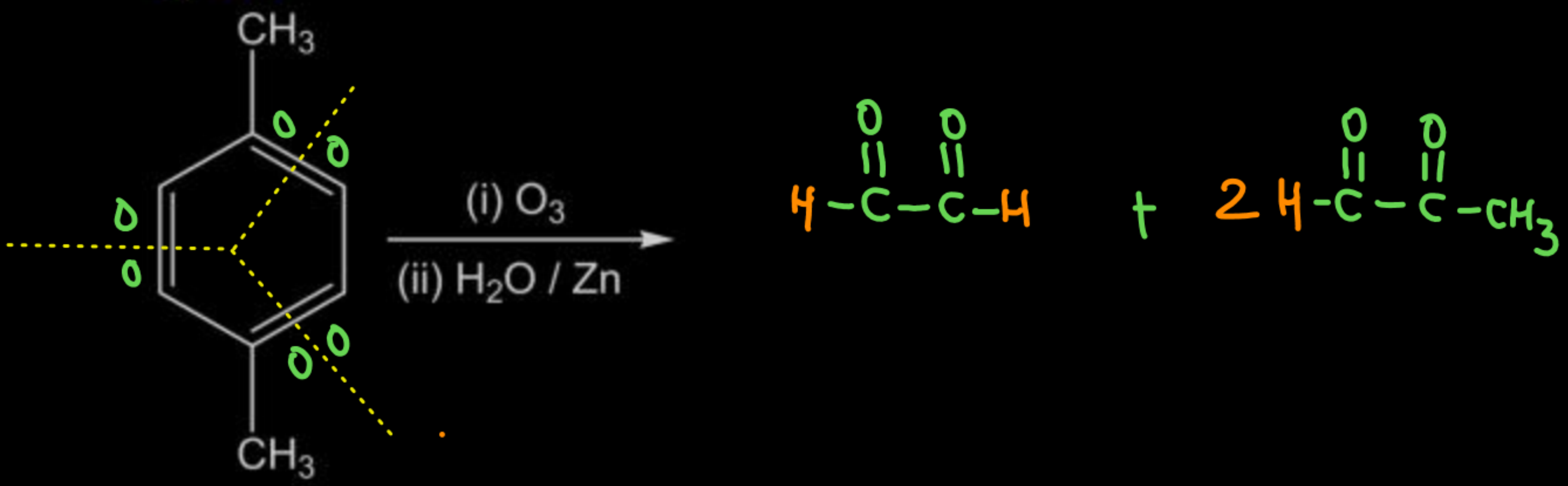


$$\xrightarrow[\text{(ii) } H_2O / Zn]{\text{(i) } O_3} H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + 2\ CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

Ques.

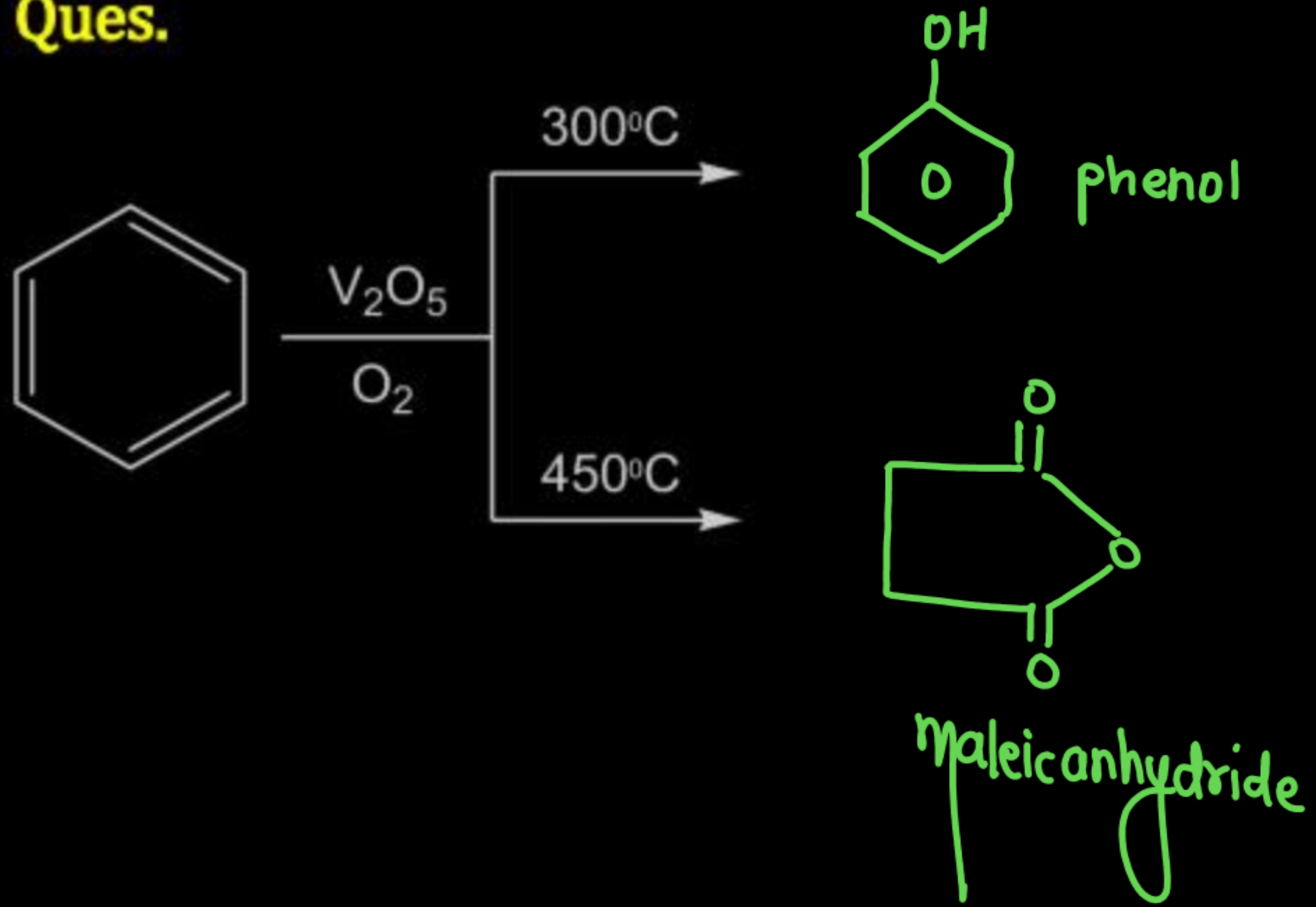

CH3
H3C
CH3
(i) O3
(ii) H2O / Zn
3
H–C–C–CH3

Ques.

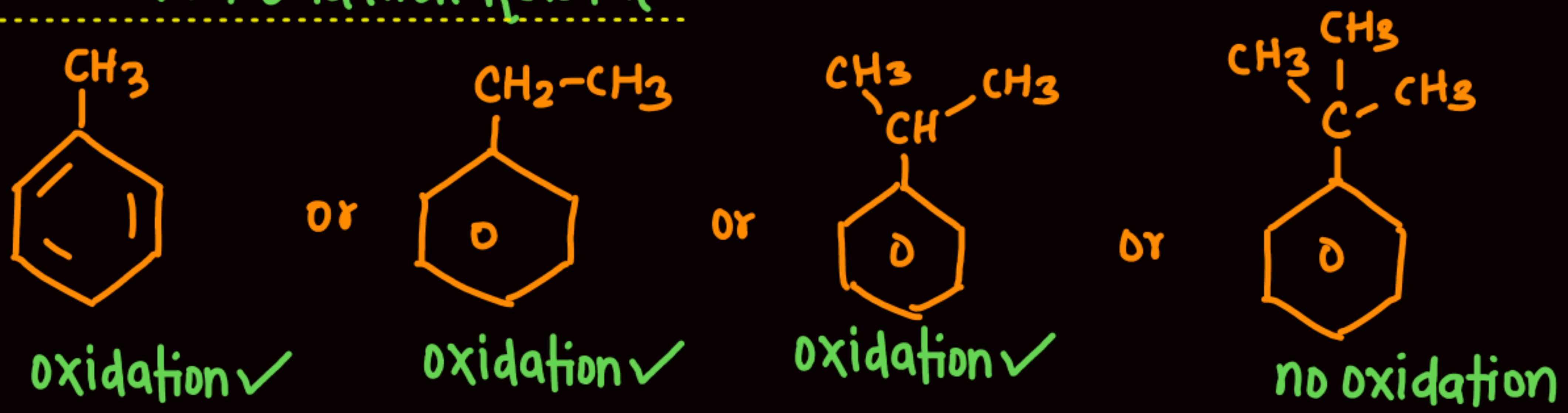

CH3
CH3
(i) O3
(ii) H2O / Zn
H–C–C–H
+
2 H–C–C–CH3

Catalytic Oxidation:

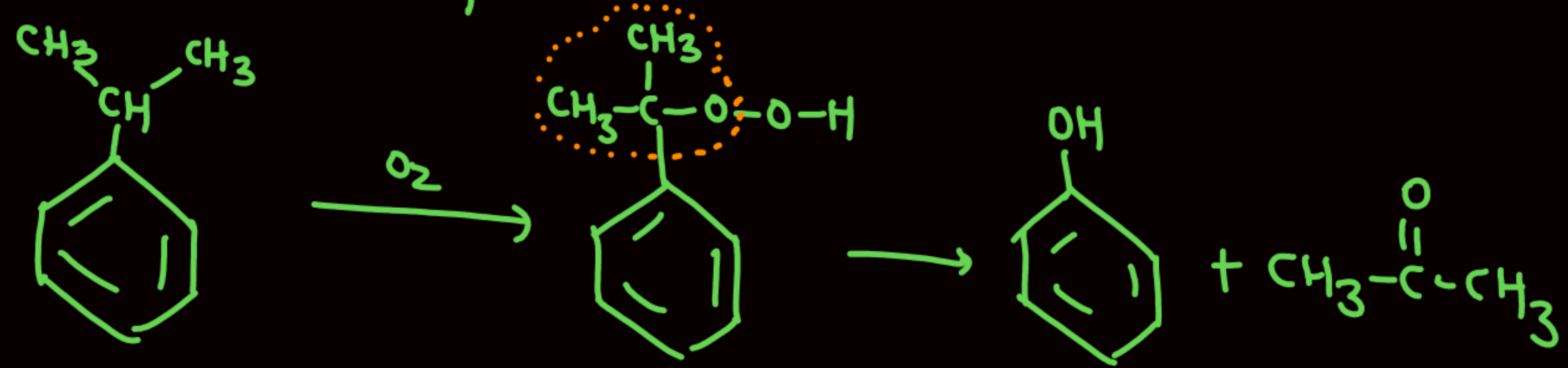
Ques.



Side chain oxidation Reaction



For oxidation presence of 'αH' is must.
Peroxide formation takes place.



THANK YOU

All the Best!! 👍

General Methods of Preparation

1. Alkane → Alkyl Halide [PPCH] Halogenation → Free Radical Substitution Reaction
2. Alkene → Alkyl Halide [X_2 addition] [HX addition]
3. Alkyne → Alkyl Halide [X_2 addition] [HX addition]
4. Alkyl Halide → Alkyl Halide [Halide exchange Reaction]
5. Alcohol → Alkyl Halide
   - (i) HCl + anhydrous $ZnCl_2$ → Lucas Reagent
   - (ii) NaBr + H_2SO_4
   - (iii) PCl_5
   - (iv) PCl_3
   - (v) Darzen Reaction
6. aldehyde/ketone → PCl_5/PBr_5
7. Carboxylic acid → Hunsdieker Reaction



Alkane ⟶ Alkyl Halide

$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3-Cl \xrightarrow[h\nu]{Cl_2} CH_2Cl_2 \xrightarrow[h\nu]{Cl_2} CHCl_3 \xrightarrow[h\nu]{Cl_2} CCl_4$$

$$CH_3-CH_3 \xrightarrow[h\nu]{Br_2} CH_3-CH_2-Br$$

<u>note</u> → Bromination is a selective Reaction [Higher degree Product]
Chlorination is a non selective Reaction.

$$CH_3-CH_2-CH_3 \xrightarrow[h\nu]{Br_2} CH_3-\underset{}{\overset{Br}{\overset{|}{C}}}H-CH_3 + CH_3-CH_2-CH_2Br$$

Major — Minor

$$\xrightarrow[h\nu]{Cl_2} CH_3-\underset{\underset{Cl}{|}}{C}H-CH_3 + CH_3-CH_2-CH_2-Cl$$

2×3.8 — 6×1

7.6 — 6

Major — Minor

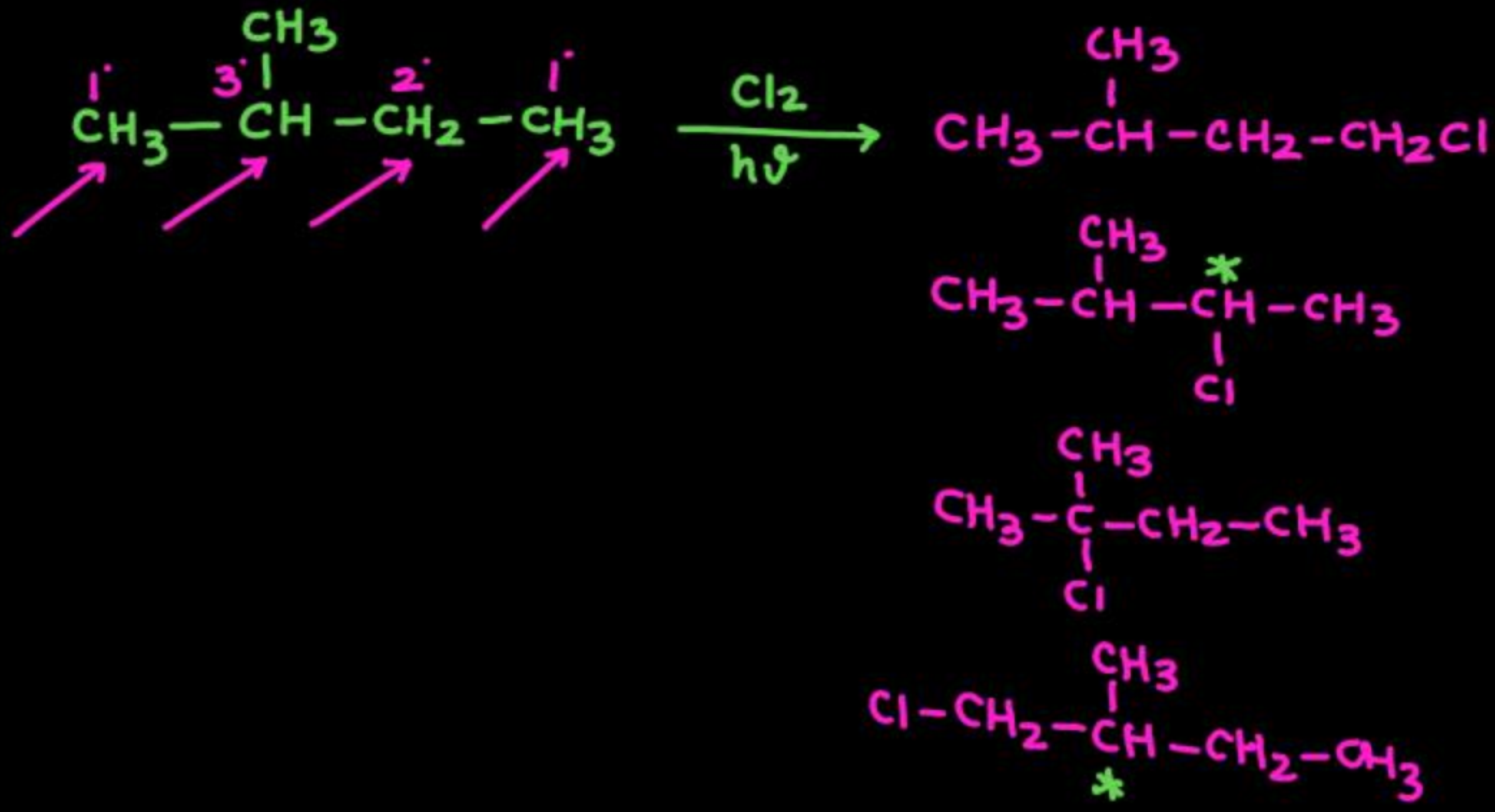
<u>note</u> → Fluorination is a very Highly Reactive reaction & exothermic.

$$CH_4 + F_2 \longrightarrow \underset{black}{C} + HF$$

* note iodination is a slow & Reversible process. (→ we need oxidising agent.)

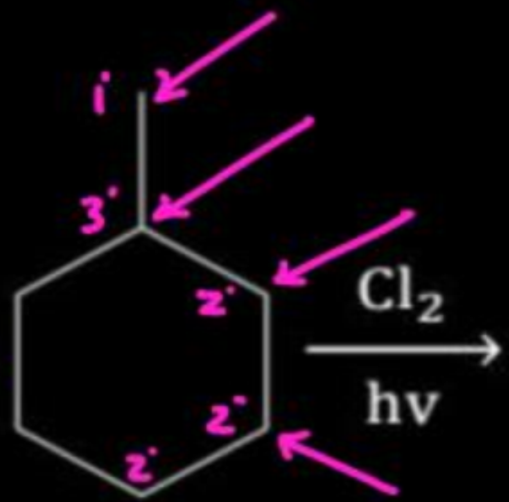
$$CH_4 + I_2 \underset{dil\,HNO_3 / dil\,HIO_3}{\rightleftharpoons} CH_3I + HI \text{ (endothermic)}$$

Ques. How many monochloro products are formed of $(CH_3)_2CHCH_2CH_3$

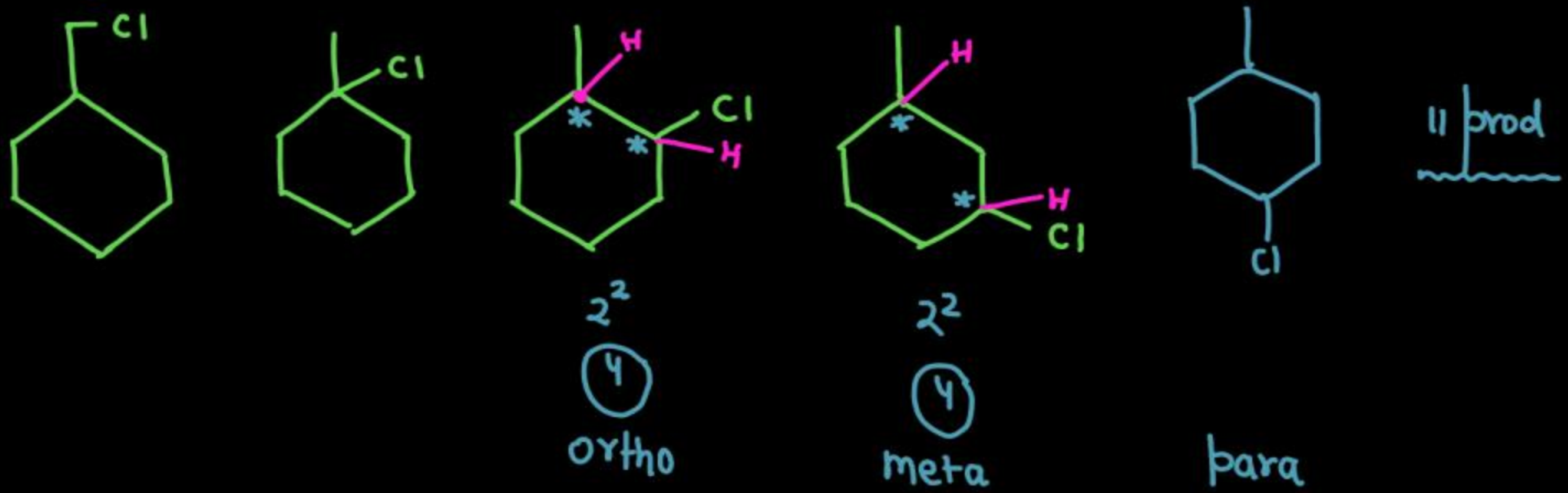


6 product

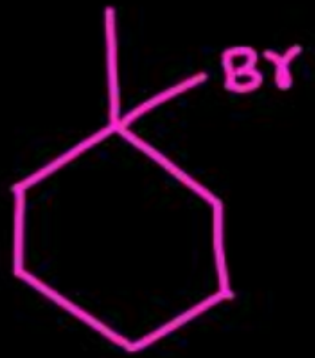


Ques. 

How many monochloro products are formed?



Ques.  $\xrightarrow[h\nu]{Br_2}$ How many monobromo (major) products are formed?



Alkene ⟶ Alkyl Halide

t.me/VTSIR1

$CH_3-CH=CH_2 \xrightarrow[CCl_4]{Br_2} Br^+\ Br^-$ → $CH_3-CH(Br)-CH_2Br$

$\xrightarrow[H_2O]{Br_2} Br^+\ OH^-$ → $CH_3-CH(OH)-CH_2Br$

$\xrightarrow[CH_3OH]{Br_2} Br^+\ {}^-OCH_3$ → $CH_3-CH(OCH_3)-CH_2Br$

(non classical carbocation)
(anti addition)

note → $\xrightarrow[\text{Peroxide}]{HBr}$ AMKRule → Peroxide effect, Kharash effect

$\xrightarrow[\text{Peroxide}]{HCl}$ MKRule

$CH_3-CH=CH_2 \xrightarrow[CCl_4]{HCl} CH_3-\overset{+}{C}H-CH_3$ → $CH_3-CH(Cl)-CH_3$

$\xrightarrow[H_2O]{HCl}$,, → $CH_3-CH(OH)-CH_3$

$\xrightarrow[CH_3OH]{HCl}$,, → $CH_3-CH(OCH_3)-CH_3$

(Carbocation)
↳ Rearrange
↳ nu⁻ attack

$CH_3-CH(CH_3)-CH=CH_2 \xrightarrow[CCl_4]{HBr} CH_3-C(CH_3)(Br)-CH_2-CH_3$

$\xrightarrow[H_2O]{HBr} CH_3-C(CH_3)(OH)-CH_2-CH_3$

$\xrightarrow[CH_3OH]{HBr} CH_3-C(CH_3)(OCH_3)-CH_2-CH_3$

AMKRule $\xrightarrow[R_2O_2]{HBr} CH_3-CH(CH_3)-CH_2-CH_2Br$
(peroxide)

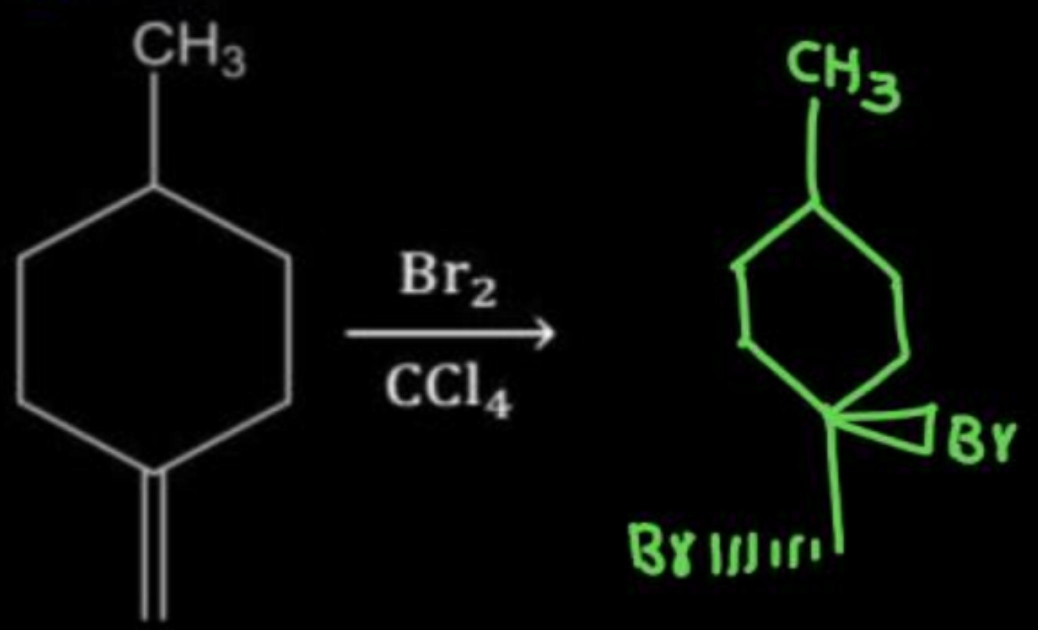
Ques.

$$CH_3-CH=CH_2 \xrightarrow[\text{aq NaCl}]{Br_2}$$

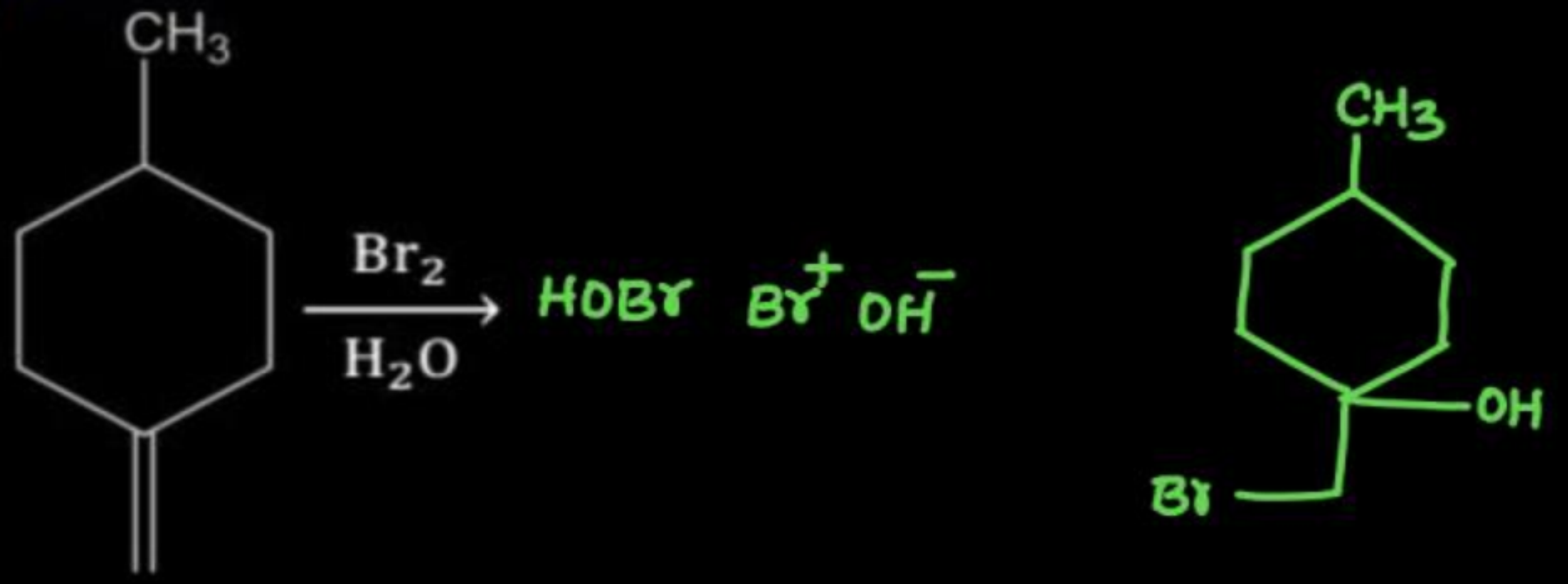
Br^+, OH^-, Cl^-, Br^-

$CH_3-CH(OH)-CH_2Br$ $\quad$ $CH_3-CH(Cl)-CH_2Br$ $\quad$ $CH_3-CH(Br)-CH_2Br$

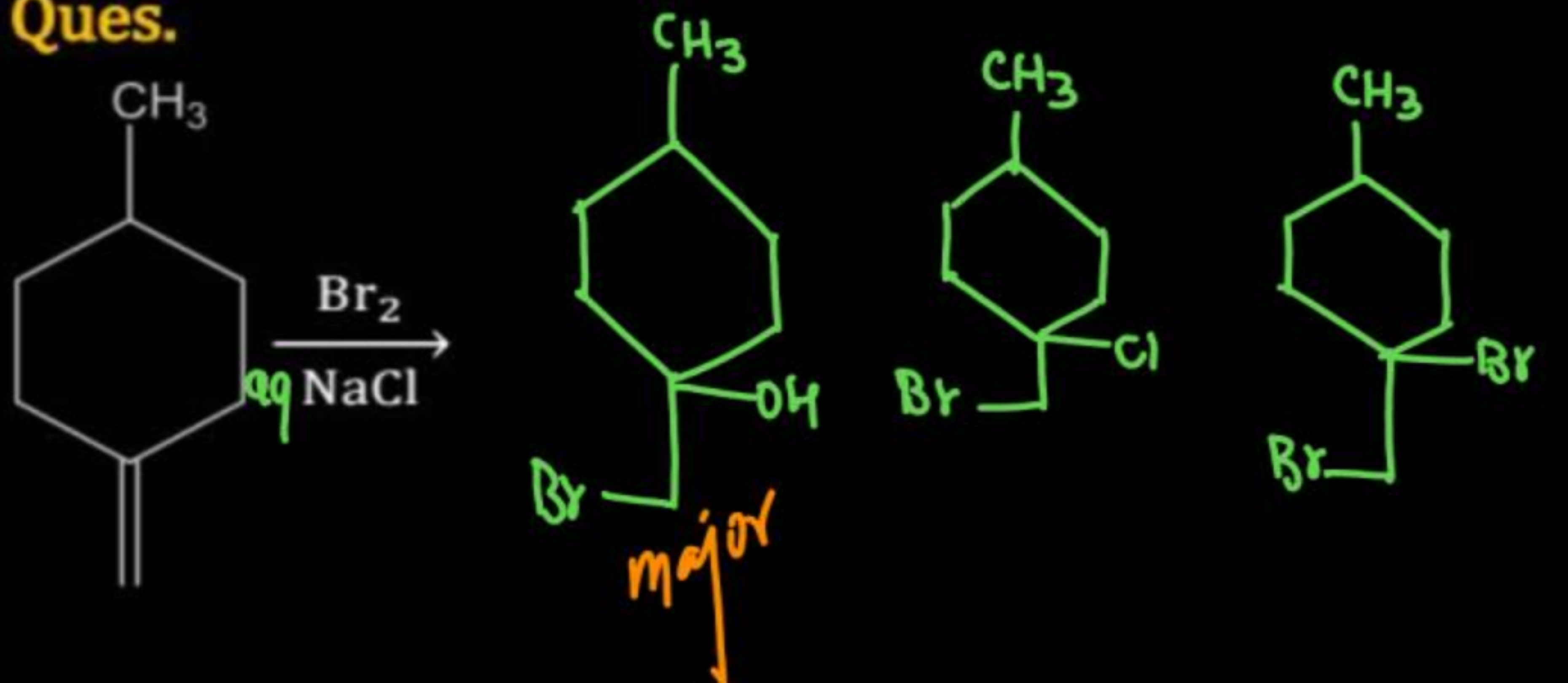
Ques.



Ques.


CH3
Br2
H2O
HOBr
Br+ OH−
CH3
OH
Br

Ques.


CH3
Br2
aq NaCl
CH3
OH
Br
major
CH3
Cl
Br
CH3
Br
Br

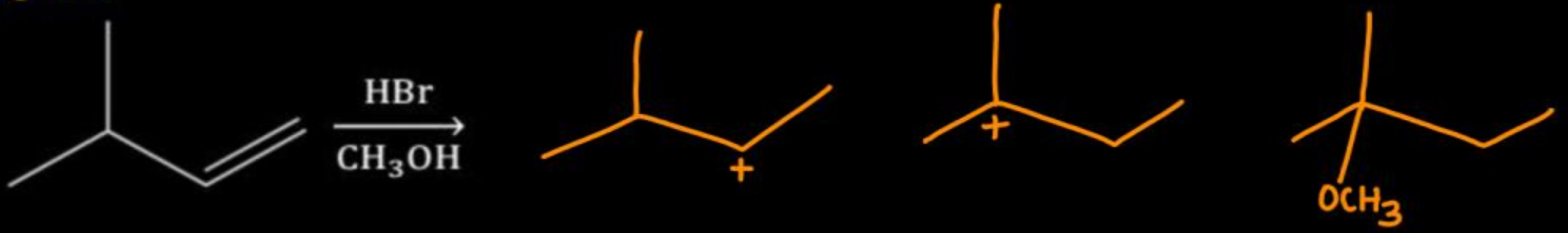
Ques.



Ques.



Ques.



Ques.

$$CH_3-\overset{\overset{\large CH_3}{|}}{C}=CH_2 \xrightarrow[H_2O_2]{HBr} CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_2Br$$

Ques.

$$CH_3-\overset{\overset{\large CH_3}{|}}{C}=CH_2 \xrightarrow[H_2O_2]{HCl} CH_3-\underset{\oplus}{\overset{\overset{\large CH_3}{|}}{C}}-CH_3 \qquad CH_3-\underset{\underset{\large Cl}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-CH_3$$



Alkyne ⟶ Alkyl Halide

$$CH_3-C\equiv CH \xrightarrow[CCl_4]{HCl} CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_3$$

$$\xrightarrow[CCl_4]{HBr} CH_3-\overset{Br}{\underset{Br}{C}}-CH_3$$

$$\xrightarrow[CCl_4]{Br_2} CH_3-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}H$$

$$\xrightarrow[CCl_4]{Cl_2} CH_3-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{C}}H$$

$$CH_3-\overset{CH_3}{CH}-C\equiv CH$$

Br^+ Br^-

$$\xrightarrow[CCl_4]{Br_2} CH_3-\overset{CH_3}{CH}-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}H$$

H^+ Br^-

$$\xrightarrow[CCl_4]{HBr} CH_3-\overset{CH_3}{CH}-\overset{Br}{\underset{Br}{C}}-CH_3$$

Br^+ OH^-

$$\xrightarrow[H_2O]{Br_2} CH_3-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-CHBr_2$$

H^+ OH^-

$$\xrightarrow[H_2O]{HBr} CH_3-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-CH_3$$

Br^+ OCH_3

$$\xrightarrow[CH_3OH]{Br_2} CH_3-\overset{CH_3}{CH}-\overset{OCH_3}{\underset{OCH_3}{C}}-CHBr_2$$

H^+ $^-OCH_3$

$$\xrightarrow[CH_3OH]{HBr} CH_3-\overset{CH_3}{CH}-\overset{OCH_3}{\underset{OCH_3}{C}}-CH_3$$



Alkyl Halide ⟶ Alkyl Halide

(i) $R-Cl$ or $R-Br$ $\xrightarrow[\text{dry acetone}]{NaI}$ $R-I$ + $NaCl$ or $NaBr$ Finkelstein Rx^n [Halide exchange Reaction]

note → dry acetone is used for precipitation of NaCl & NaBr.

(ii) $R-Cl$ or $R-Br$ $\xrightarrow{SbF_3 / AgF / Hg_2F_2 / CoF_2}$ $R-F$ Swart's Reaction [Halide exchange Reaction]

Q $CH_3-\underset{Cl}{\underset{|}{C}H}-CH_3 \xrightarrow{AgF} CH_3-\underset{F}{\underset{|}{C}H}-CH_3$ + AgCl (white ppt)

Q $CH_3-CH_2-CH_2-Br \xrightarrow{AgF} CH_3-CH_2-CH_2-F$ + AgBr (light yellow ppt)

$\xrightarrow[\text{acetone}]{NaI} CH_3-CH_2-CH_2-I$



Alcohol ⟶ Alkyl Halide

(i) Lucas Reagent

$$CH_3-CH_2-CH_2-\ddot{O}H \xrightarrow[\text{anhy } ZnCl_2]{\text{Conc HCl}} CH_3-CH_2-CH_2^{\oplus} \longrightarrow CH_3-\overset{\oplus}{C}H-CH_3 \longrightarrow CH_3-\overset{Cl}{\overset{|}{C}H}-CH_3$$

ppt form

→ anhy $ZnCl_2$ → absorbs H_2O.

→ Carbocation → Rearrange → ⊖ attack

$$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-OH \xrightarrow[\text{anhy } ZnCl_2]{HCl} CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2^{\oplus} \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{\oplus}{C}}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_3$$

ppt form

→ **HCl + anhydrous $ZnCl_2$** → Lucas Reagent

3° alcohol $\xrightarrow{HCl + ZnCl_2}$ Fastest Reaction → immediate ppt for.

2° alcohol $\xrightarrow{\quad " \quad}$ → 5 min ppt Form

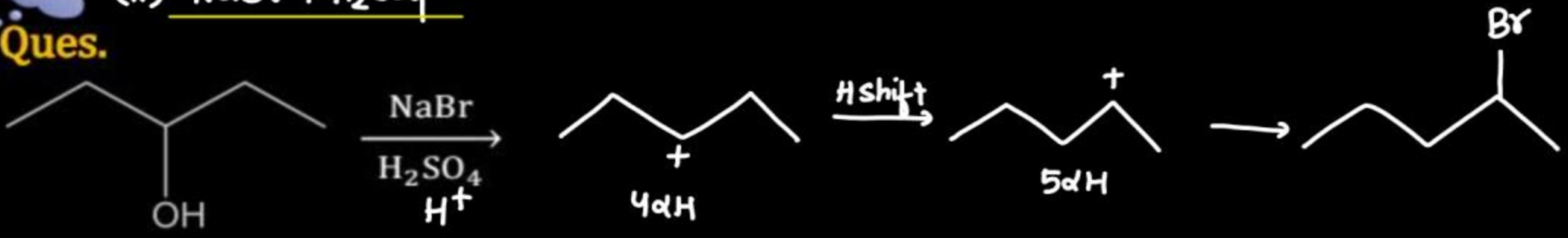
1° alcohol $\xrightarrow{\quad " \quad}$ slow Reaction → 30 min ppt form.

3° alcohol > 2° alcohol > 1° alcohol → Rate of Rxn.

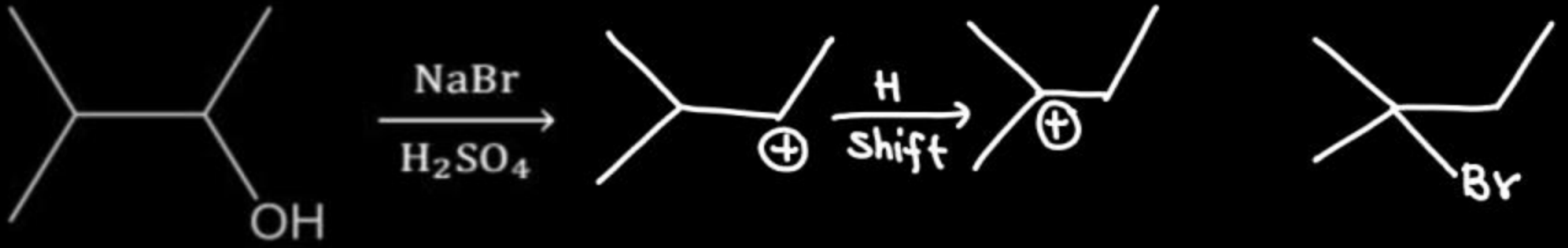
HI > HBr > HCl > HF → Rate of Rxn

(ii) NaBr + H_2SO_4

Ques.



Ques.

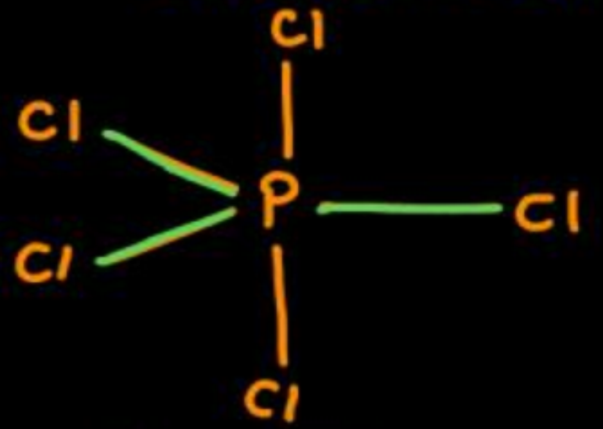




Alcohol ⟶ Alkyl Halide

(iii) PCl_5 Reaction

5σ bond → sp^3d

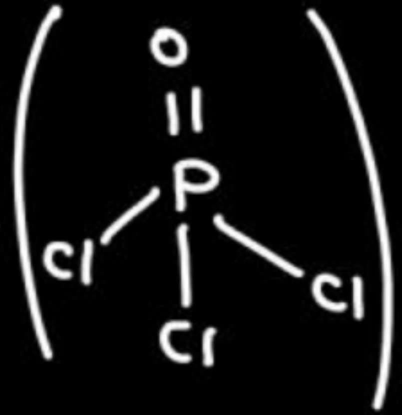


$\xrightarrow{\Delta} PCl_3 + Cl_2$

2 axial bond → Weak bond → Large bond length
3 Equitorial bond → Strong bond → Small bond length

$CH_3-CH_2-OH + PCl_5 \longrightarrow CH_3-CH_2-Cl + POCl_3$

(PCl_5 ↓ $\ddot{P}Cl_3 + Cl_2$; H–Cl)

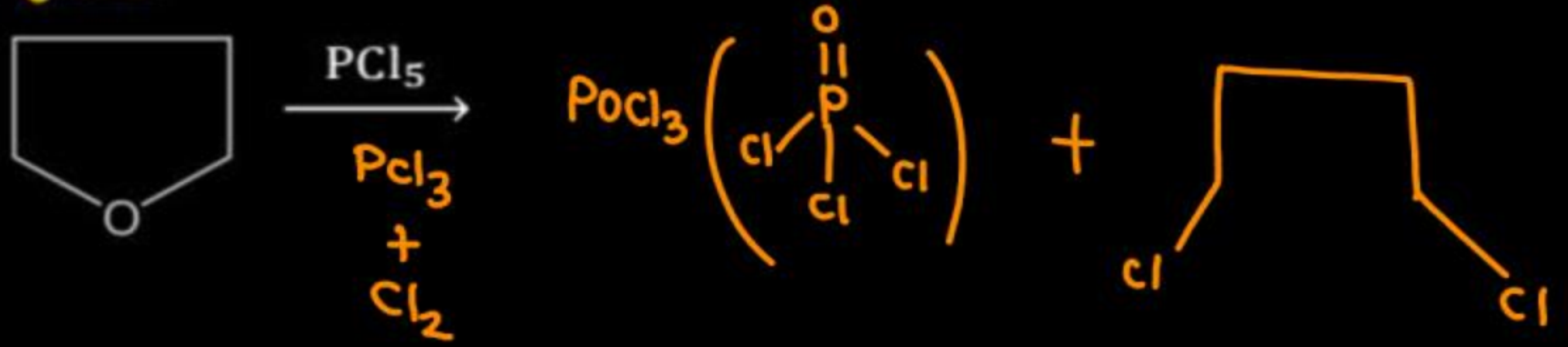




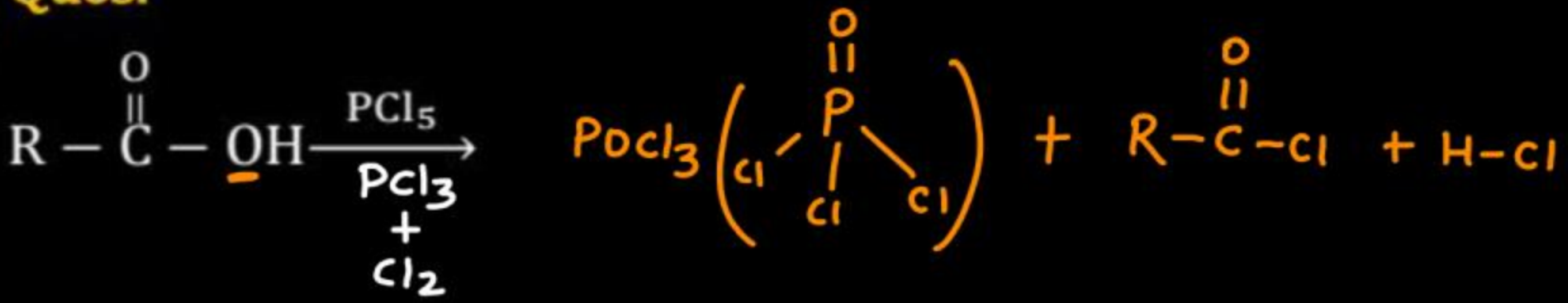
Ques.

$$CH_3 - CH_2 - OH \xrightarrow{PCl_5}$$ ✓

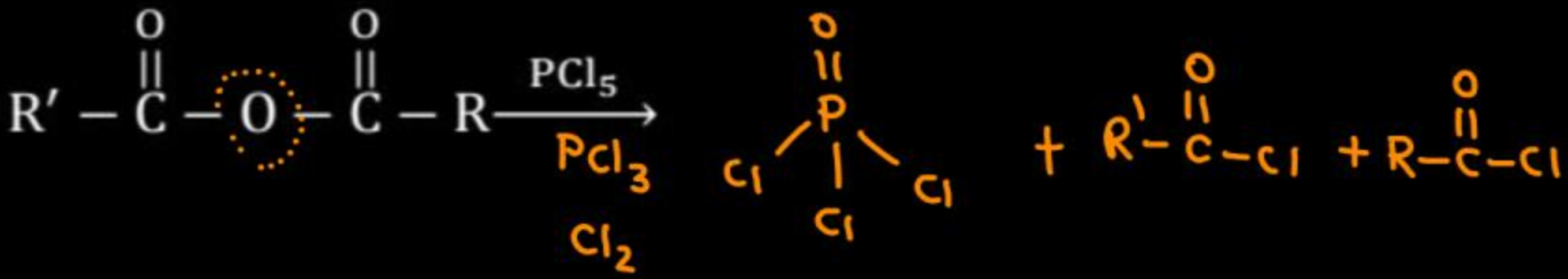
Ques.



Ques.



Ques.

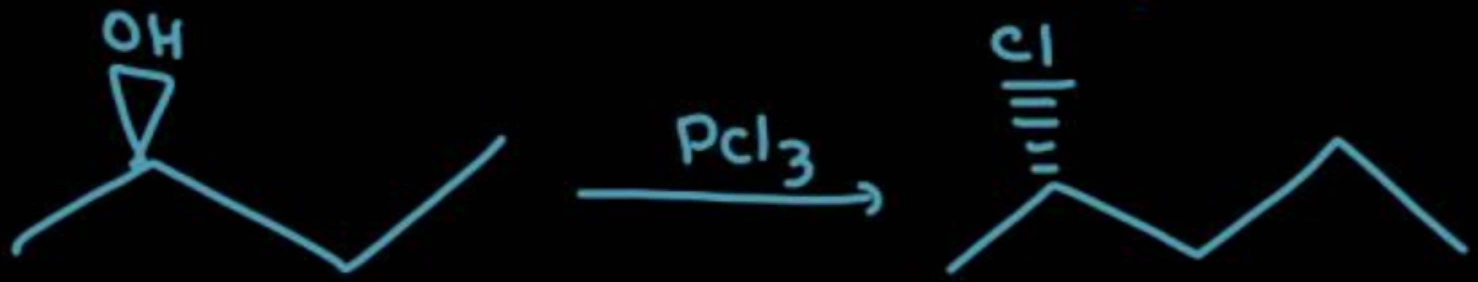


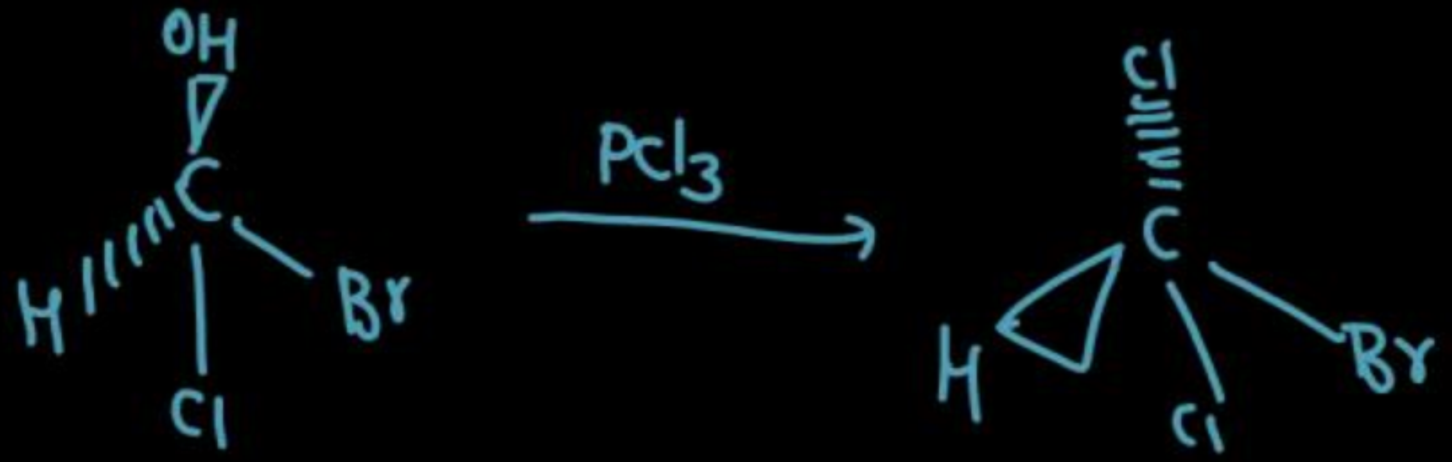
Reaction with PCl_3

$$CH_3-CH_2-OH \xrightarrow{PCl_3} CH_3-CH_2-Cl$$

* anti addition of 'Cl' takes place.









Reaction with $SOCl_2$

Darzen Reaction

$$CH_3-CH_2-OH + SOCl_2 \longrightarrow CH_3-CH_2-Cl + SO_2\uparrow + HCl\uparrow$$

CH_3-CH_2-Cl: good yield

$SO_2\uparrow + HCl\uparrow$: gaseous product
↓
easily escapes from Reaction

This reaction is preferred for preparation of alkyl chloride.
Bcoz products are gaseous & easily escape from rxn.
& product yield is good.

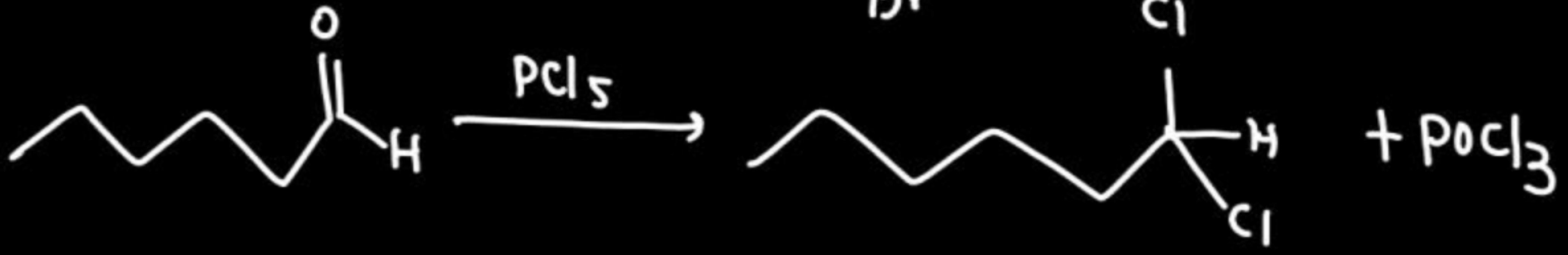
From Aldehyde/Ketone: -

Ques.

$$H_3C-\overset{\overset{O}{\|}}{C}-H \xrightarrow[PBr_3 + Br_2]{PBr_5} CH_3-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-H + POBr_3$$

Ques.

$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{PBr_5} CH_3-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3 + POBr_3$$





Carboxylic Acid

$$CH_3-\overset{\overset{O}{||}}{C}-O^-Ag^+ \xrightarrow[CCl_4]{Cl_2} CH_3-Cl + CO_2 + AgCl$$

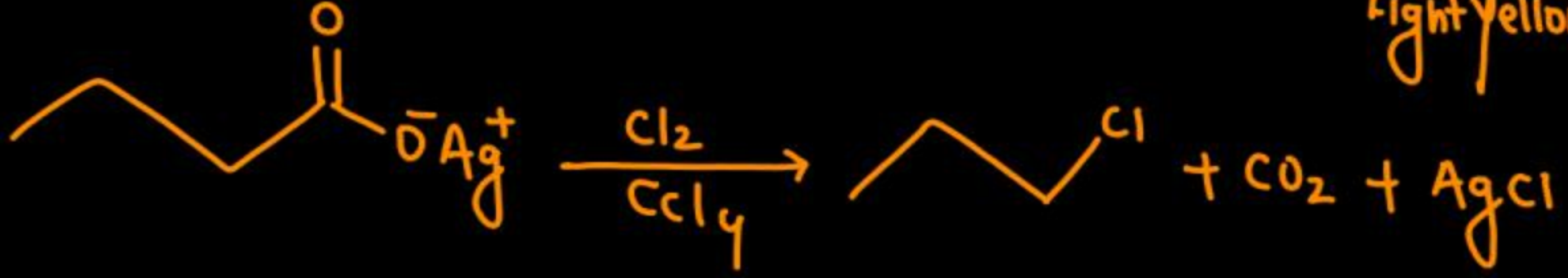
Silver Salt of Carboxylic acid

(Hunsdiecker Reaction)

AgCl: White ppt

$$\text{,,} \xrightarrow[CCl_4]{Br_2} CH_3-Br + CO_2 + AgBr$$

AgBr: Light Yellow ppt



→ Step down rx^n

→ prod is alkyl halide

→ ppt of Silver salt.

Chemical Reaction of Alkyl Halide

1. Nucleophilic substitution → SN^1 & SN^2

2. Elimination Reaction → E^1 & E^2

3. Reaction with Metal

Nucleophilic Substitution Reaction

$$Nu^- + \overset{\delta+}{R} - \overset{\delta-}{X} \xrightarrow{\text{Solvent}} R{-}Nu + X^-$$

['X' is Substituted by Nu^-]

Substrate Leaving Group

Eg

$$OH^- + \overset{\delta+}{CH_3} - \overset{\delta-}{Cl} \xrightarrow{H_2O} CH_3{-}OH + Cl^- \text{ (Stable)}$$

① Substrate → Species on which nucleophile attacks is called Substrate.

② Leaving group → Stable species which leaves from the reaction is called Leaving group.

Leaving Group tendency ∝ Stability of anion

$\propto \dfrac{1}{\text{basic strength}}$

$F^- < Cl^- < Br^- < I^-$ (Leaving grp tendency)

$F^- > Cl^- > Br^- > I^-$ (Basic Strength tendency)

③ Solvent : Like dissolves Like

: For alkylhalide, polar solvent is used.

Polar Solvent

Polar Protic Solvent

→ Solvent in which Hydrogen is Connected to more EN atom.

H_2O, NH_3, CH_3COOH

R–OH, R–NH_2, HCOOH

Ph–OH, Ph–NH_2

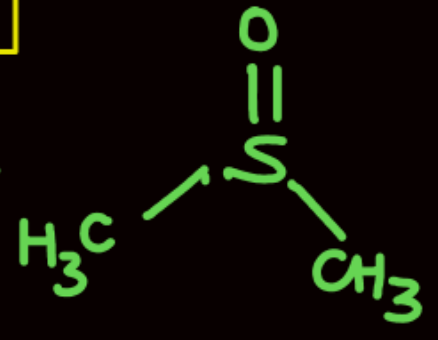
HCOOH, $HCONH_2$

→ It solvates both Cation & anion.

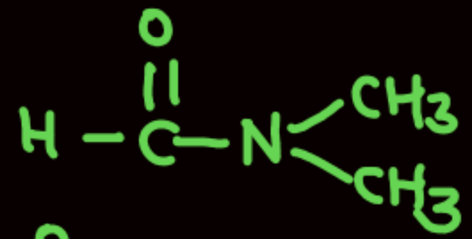


Polar Aprotic Solvent

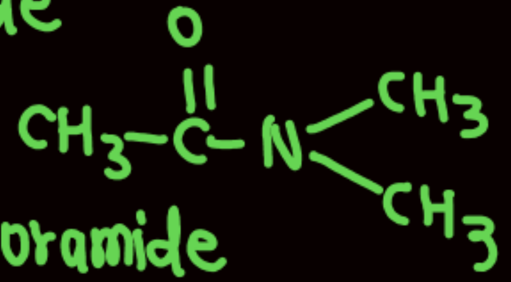
① DMSO Dimethyl sulphoxide



② DMF Dimethyl Formamide



③ DMA Dimethyl acetamide



④ HMPA Hexamethylphosphoramide



④ nucleophilicity → Tendency to donate

$$\text{nucleophilicity} \propto e^- \text{ density} \propto \frac{+M, +H, +I}{-M, -H, -I}$$

nucleophilicity (Polar protic Solvent) $\propto$ Size of donating atom

nucleophilicity (polar aprotic solvent) $\propto$ Basic Strength

Comparison of nucleophilicity: -

Ques.

$F^- < Cl^- < Br^- < I^-$ (H_2O)

$OH^- < SH^-$ (H_2O)

$PhO^- < PhS^-$ (H_2O)

$NH_3 < PH_3$ (H_2O)

$CH_3^- > NH_2^- > OH^- > F^-$ (period)

$F^- > Cl^- > Br^- > I^-$ (DMSO)

$OH^- > SH^-$ (DMA)

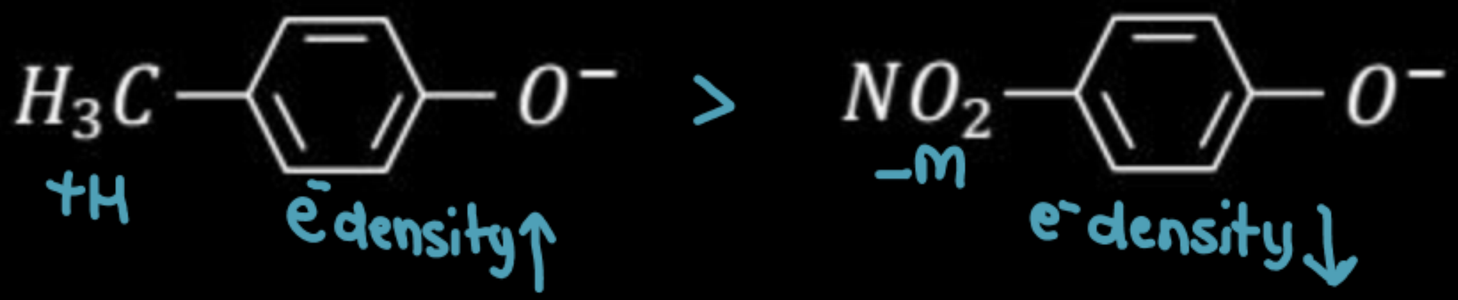
$PhO^- > PhS^-$ (HMPA)

$NH_3 > PH_3$ (DMF)

Comparison of nucleophilicity: -

Ques.

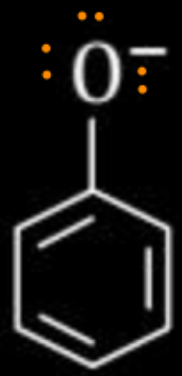
$H_3C - O^-$ > 



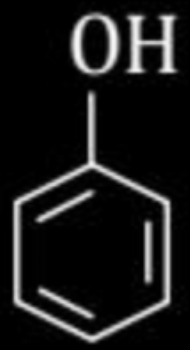
Ques.

$$H_3C - \overset{\displaystyle O}{\overset{\|}{C}} - OH \quad < \quad H_3C - \overset{\displaystyle O}{\overset{\|}{C}} - O^-$$

Ques.



>

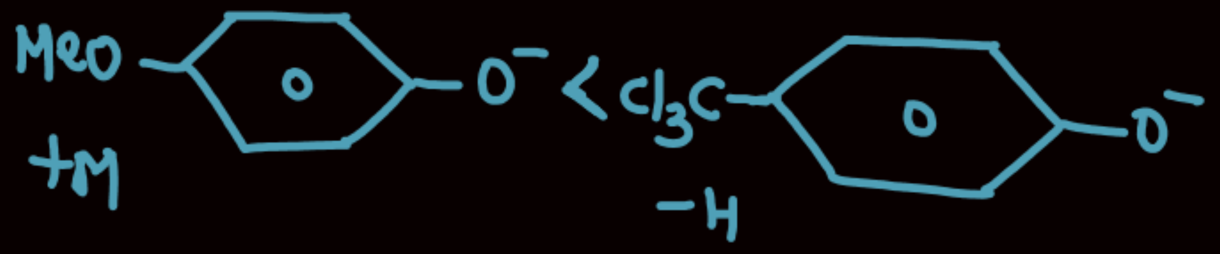


Leaving Group

Leaving Group Tendency ∝ Stability of anion

$F^- < Cl^- < Br^- < I^-$ (Leaving grp tendency)

$CH_3-CH_2^- < NO_2-CH_2^-$ (,, ,, ,,)



Nucleophilic substitution

$$Nu^{-} + \overset{\delta+}{R} - X \xrightarrow{\text{Solvent}} R - Nu + X^{-}$$

Nucleophilic substitution of Alkyl halide (R – X)

Ques.

$$\overset{\delta+}{R} - \overset{\delta-}{X} \quad + \quad NaO\overset{-}{H} \longrightarrow R-OH + NaX$$

$$\overset{\delta+}{R} - X \quad + \quad H - \overset{-}{OH} \longrightarrow R-OH + HX$$

$$\overset{\delta+}{R} - X \quad + \quad Na - \overset{-}{O}R \longrightarrow R-O-R + NaX$$

$$\overset{\delta+}{R} - X \quad + \quad Na - \overset{-}{I} \longrightarrow R-I + NaX$$

Ques.

$R - X \quad + \quad Na - I \longrightarrow$ ✓

NH_2^-

$R - X \quad + \quad NH_3 \longrightarrow \quad R{-}NH_2 + HX$

$R - X \quad + \quad R - NH_2 \longrightarrow \quad R{-}NH{-}R + HX$

$R{-}NH^-$



VVIP Ques.

$^{\ominus}:C\equiv N:$

$K^{+}\ CN^{-}$

$\delta+$

$$R-X \xrightarrow[\text{ionic bond}]{KCN} R-CN + KX$$

$$R-X \xrightarrow[AgCN: \text{ Covalent bond}]{} R-NC + AgX$$

$$R-X \xrightarrow{KNO_2} R-ONO \text{ (nitrite)}$$

$$R-X \xrightarrow{AgNO_2} R-NO_2 \text{ (nitro)} + AgX$$

$Ag^{+}\ NO_2^{-}$



Ques.

Reducing agent

$$\overset{\delta+}{R} - \overset{\delta-}{X} \xrightarrow[H^{\ominus}]{LiAlH_4} R-H$$

$$R - X \quad + \underset{\substack{\text{Grignard} \\ R'^{\ominus}}}{R'MgX} \longrightarrow R-R'$$

order=1 molecularity=1

S_N1 Reaction

→ Nucleophilic Substitution Reaction of Order 1.
→ Unimolecular Reaction.
→ S_N1 reaction only depends on [R−X]
→ Rate of S_N1 ∝ [R−X].
→ Intermediate → Carbocation
→ Rate of Reaction → $3°$ R−X > $2°$ R−X > $1°$ R−X
→ Weak Nucleophile is taken.
→ In S_N1; Nucleophile attacks from both sides i.e Racemisation product will be formed.
(Retention as well inversion)

- Retention: nu^- attacks on same side of Cl.
- Inversion: nu^- attacks from opp side of Cl.

→ In S_N1 polar protic solvent is taken (b/z in step 1 both ⊕ & ⊖ charge is formed)
→ Weak nucleophile.
→ In S_N1 Solvent acts as nucleophile.

$$CH_3-CH_2-Cl \xrightarrow[NaOH]{OH^-}$$

Step 1 Carbocation Formation.

$$\underset{(weak)}{NaOH^-} + CH_3-\overset{\delta+}{CH_2}-\overset{\delta-}{Cl} \xrightarrow{RDS} CH_3-\overset{\oplus}{CH_2} + \overset{\ominus}{Cl}$$

Step 2 Nucleophile Attack.

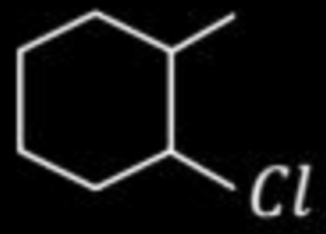
$$CH_3-\overset{\oplus}{CH_2} + Na\overset{\ominus}{O}H \longrightarrow CH_3-CH_2\blacktriangleleft OH \text{ or } CH_3-CH_2\text{''''''}OH + NaCl$$

Rate of S_{N1}

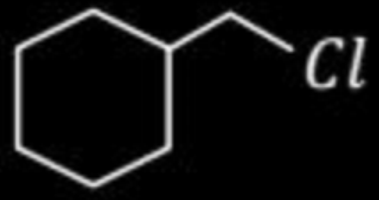
Ques.

(a) 

3°

(b) 

2°

(c) 

1°

Rate → a > b > c

Ques. (a) $H_2C = \overset{\oplus}{C}H - \ddot{B}r:$

Resonance stable → donot break easily.

(b) $H_2C = CH - \overset{\oplus}{C}H_2 - Br$

easily breakdown

Rate → b > a

Ques.

(a) 

(+H)

(b) 

(c) 

(−M)

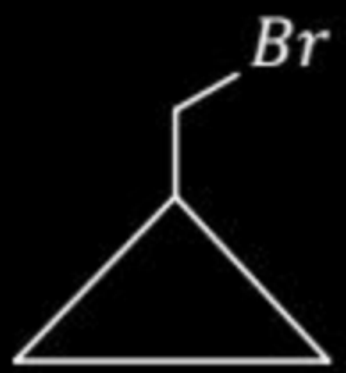
a > b > c

Ques. $H_3C - \ddot{\underset{..}{O}} - \overset{\oplus}{C}H_2 - Br$ $\qquad$ $H_3C - \overset{+}{C}H_2 - Br$ $\qquad$ Rate → a>b

pπ - pπ Reso

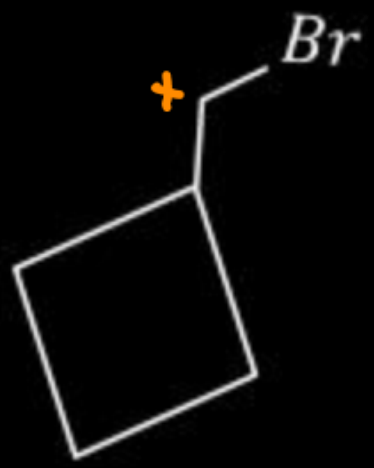
es. H_3

Ques.



cpm cation

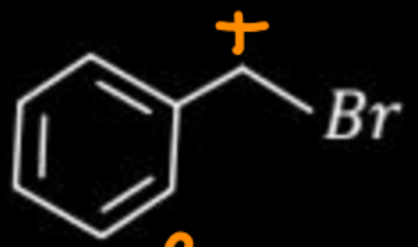
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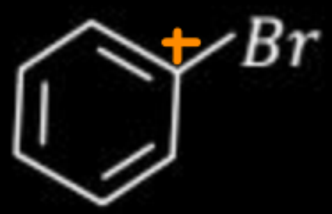
Rate → a>b



Ques.



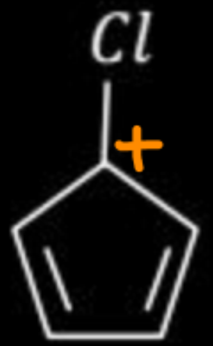
Resonance



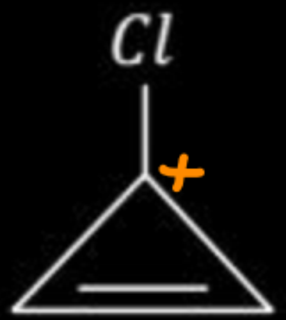
Unstable Carbocation

a > b

Ques.



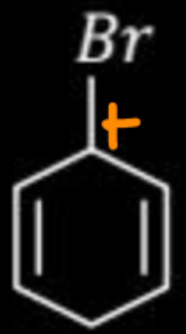
$4\pi e^-$
Anti Aromatic



$2\pi e^-$
Aromatic

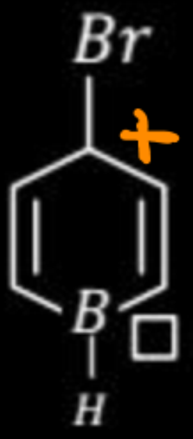
b > a

Ques.





+m



-m

b > a > c

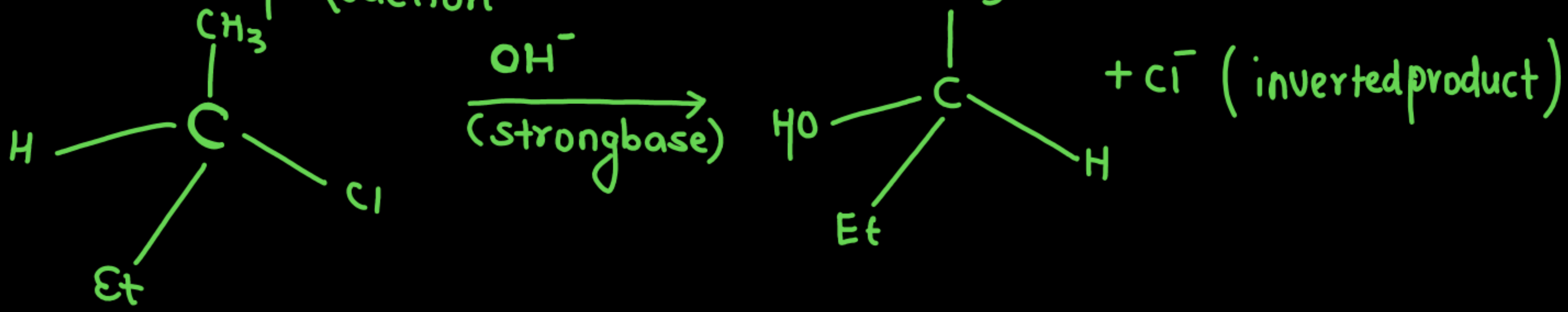
THANK YOU

All the Best!! 👍

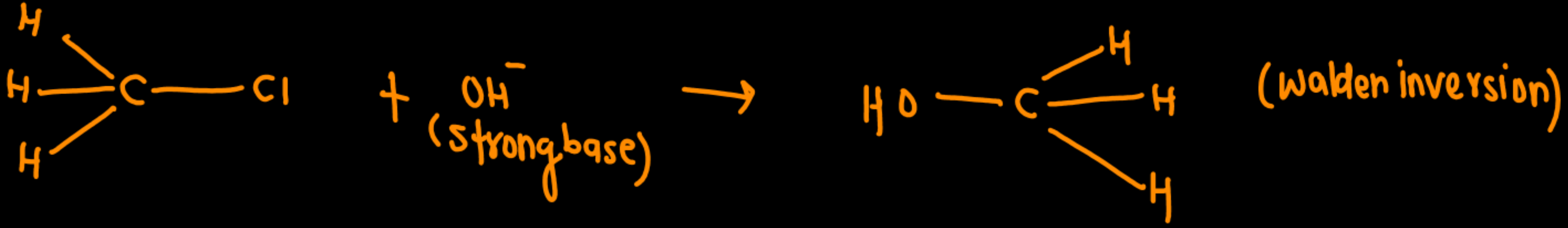
SN^2 Mechanism



- order = 2
- Nucleophilic Substitution
- Bimolecular Reaction
- Rate $\propto$ [R–X] [Nu^-]
- one step Reaction



- Back Side attack takes place. (This is known as inversion) (walden inversion)



$$\text{Rate of } S_N2 \propto \frac{1}{\text{Steric crowding}}$$

$1^\circ R-X < 2^\circ R-X < 3^\circ R-X$ (S_N1)

$1^\circ R-X > 2^\circ R-X > 3^\circ R-X$ (S_N2)

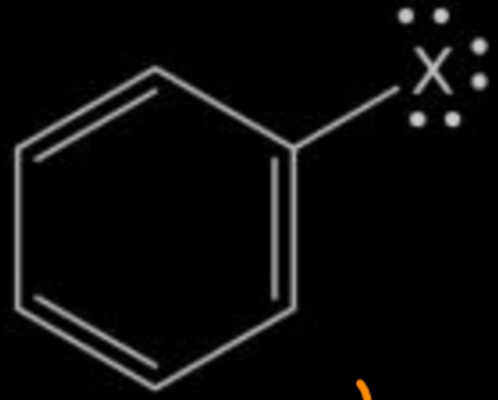
- NO carbocation is formed in the reaction.
- polar aprotic solvent is used.

Few Compounds which do not give S_N2:

Ques.



Resonance → double bond character → Strong Bond



↓ Reso → DBC → Strong Bond



Bridgehead Carbon

Rate of S_N2:

Ques.

H_3C-Cl $\quad$ H_3C-CH_2-Cl $\quad$ $H_3C-CH(CH_3)-Cl$ $\quad$ $H_3C-C(CH_3)_2-Cl$

a > b > c > d

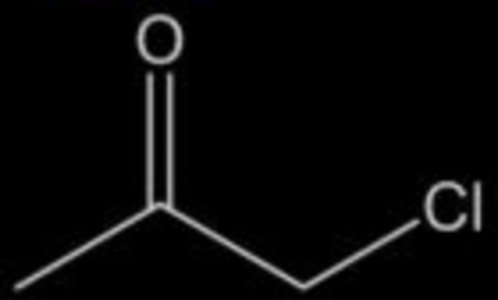
Ques.

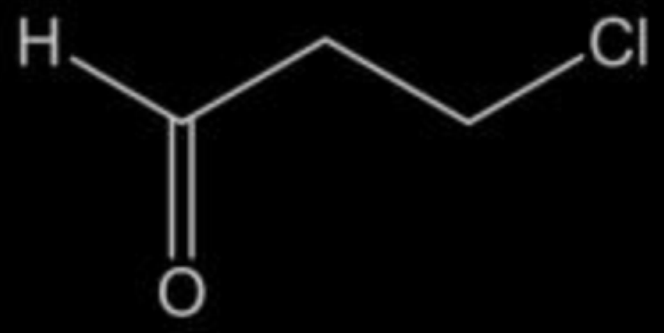




a > b

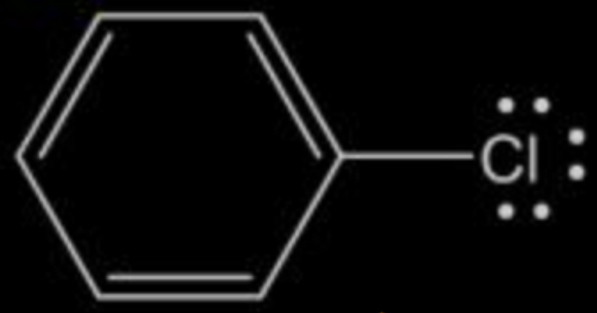
Ques.

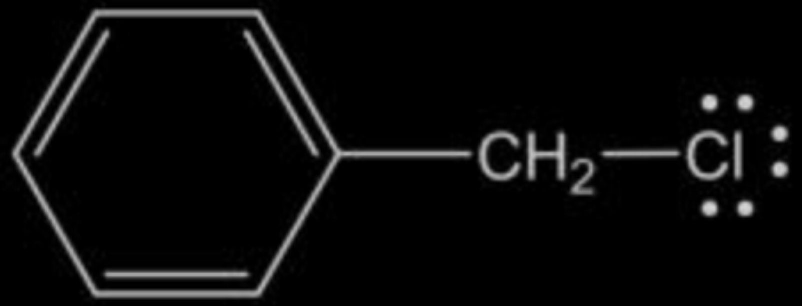




a > b

Ques.

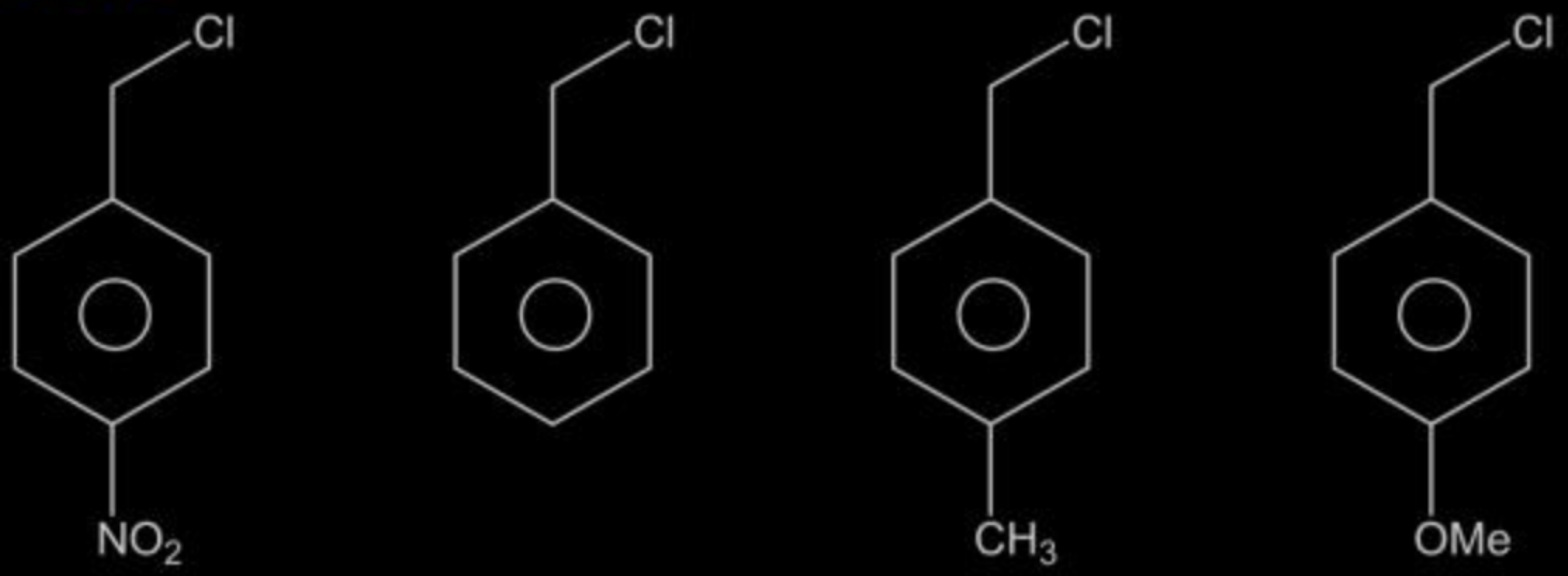




b>a

↓
This will not give SN^2

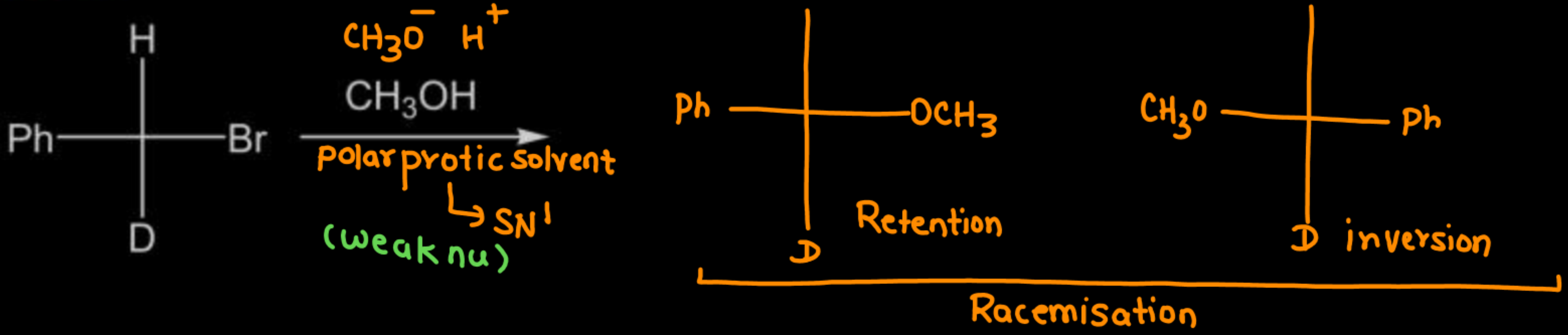
Ques.



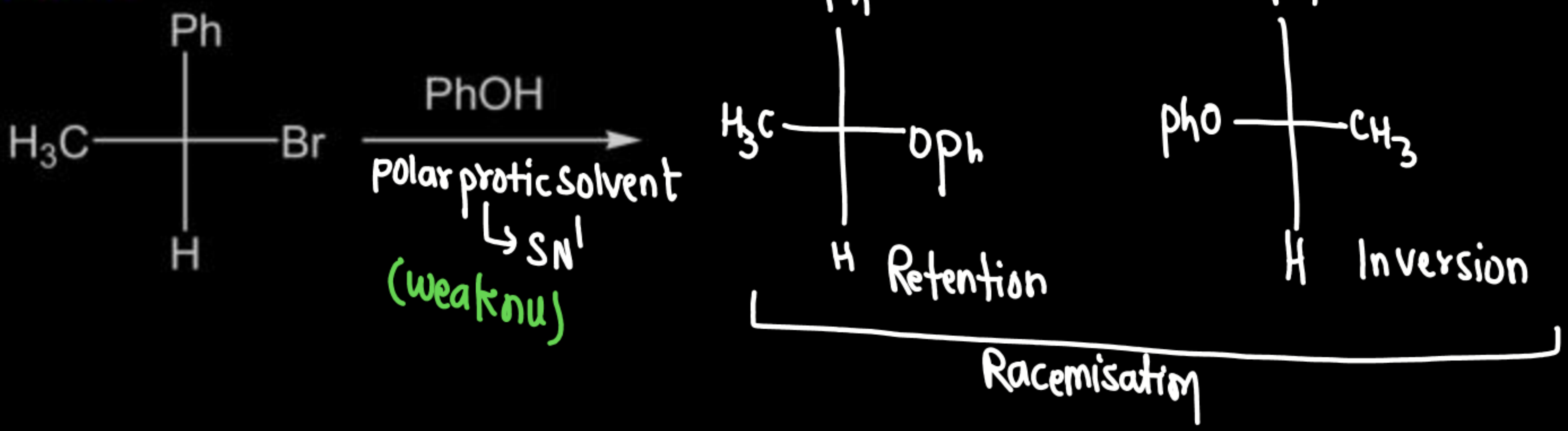
a > b > c > d

Identify the S_N1 and S_N2 reaction and find the product:

Ques.

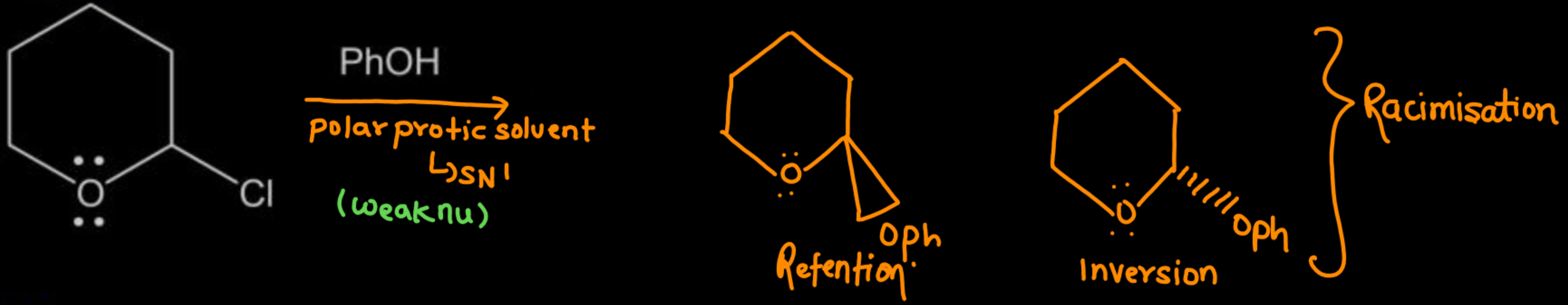


Ques.

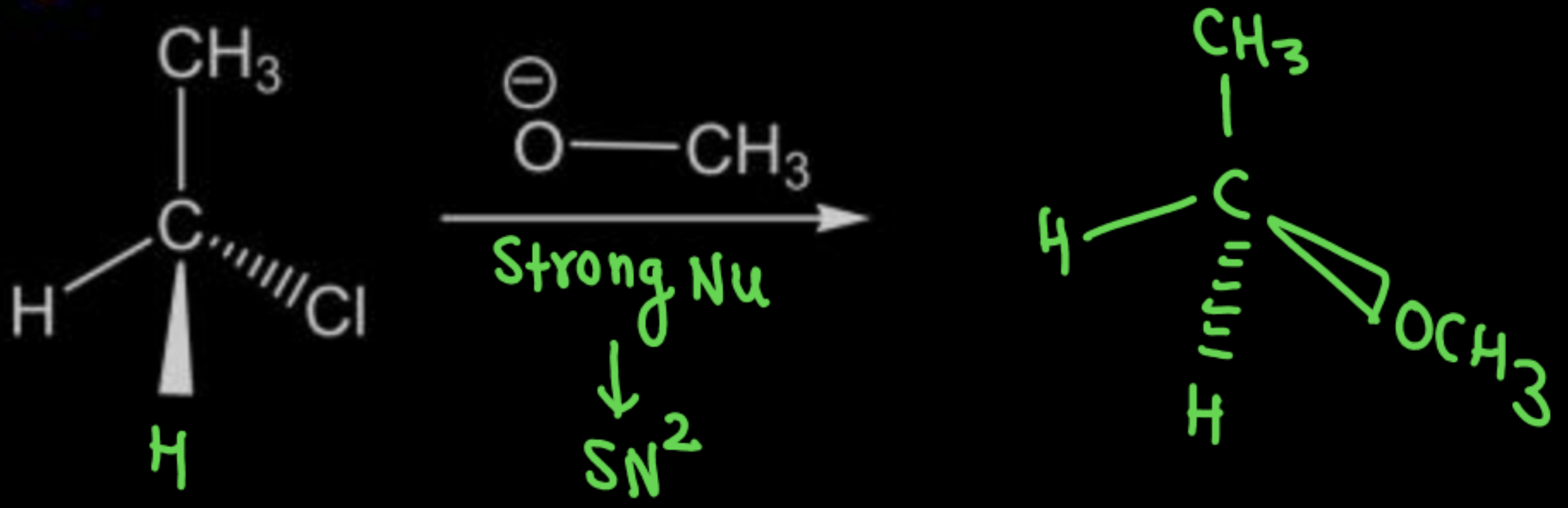


NOTE → In SN' reaction, weak nucleophile is taken (Solvent acts as nucleophile)

Ques.

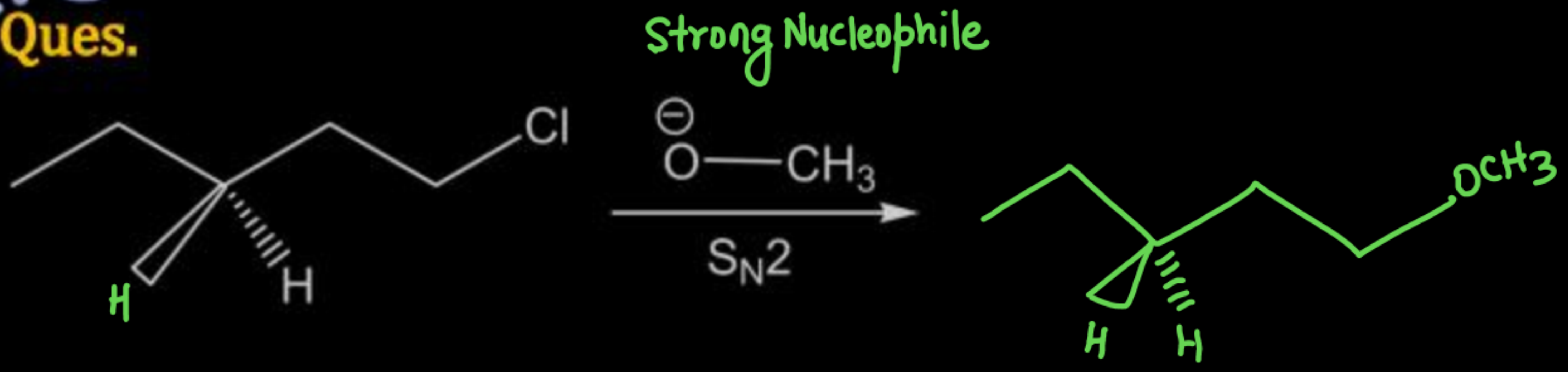


Ques.

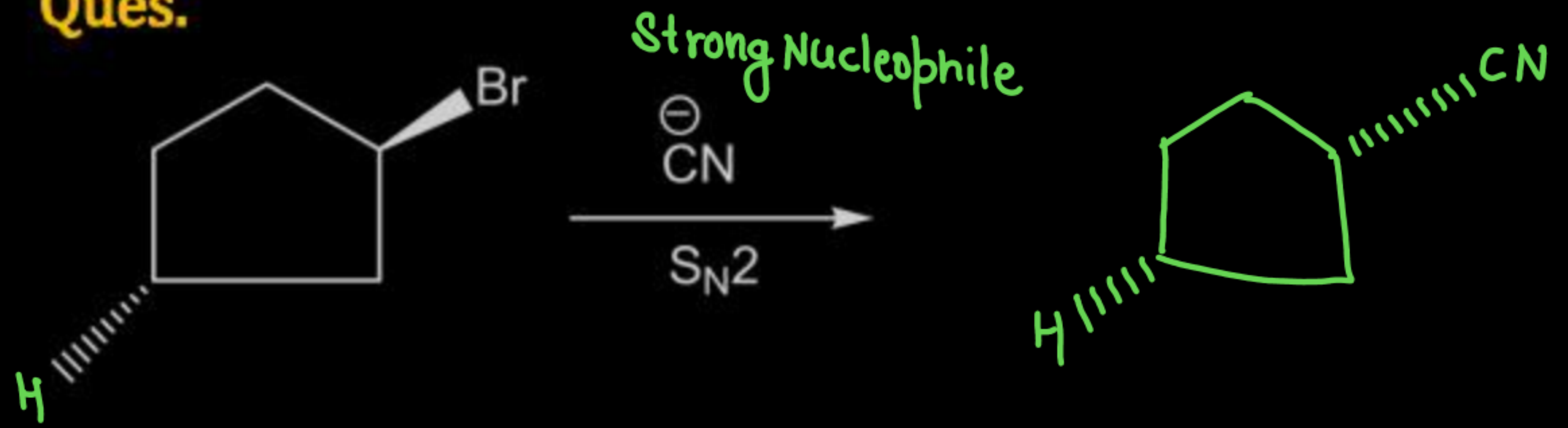


inverted product

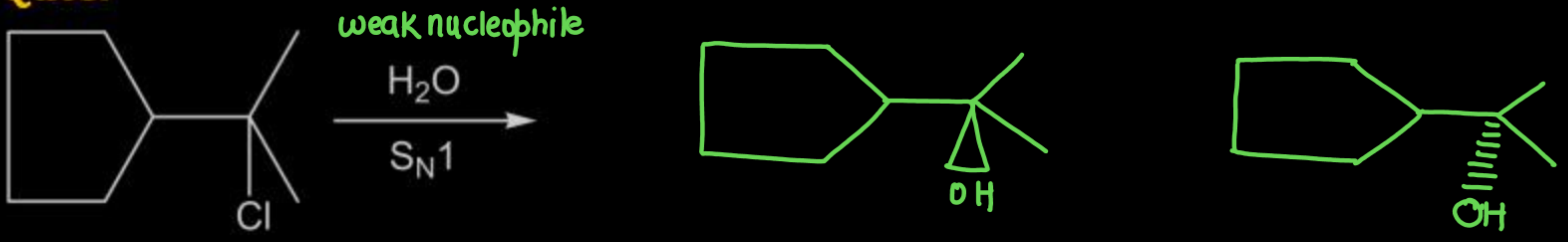
Ques.


Cl
H
H
Strong Nucleophile
O—CH3
SN2
OCH3
H
H

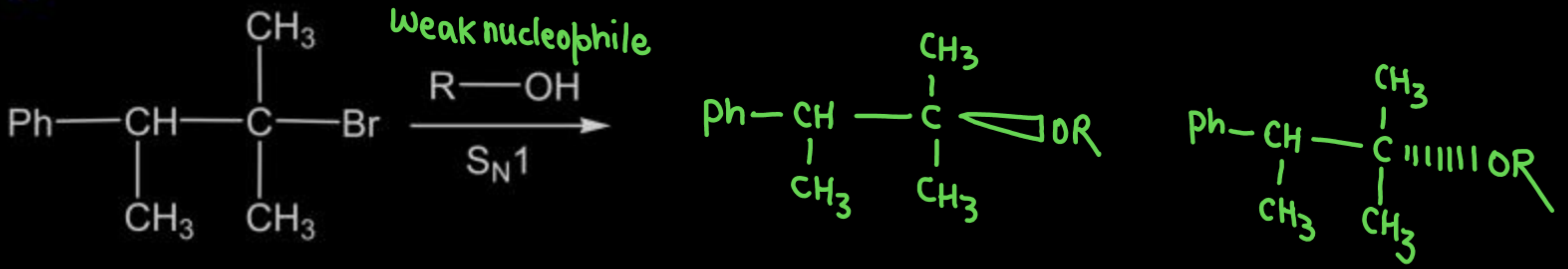
Ques.


Br
H
Strong Nucleophile
CN
SN2
CN
H

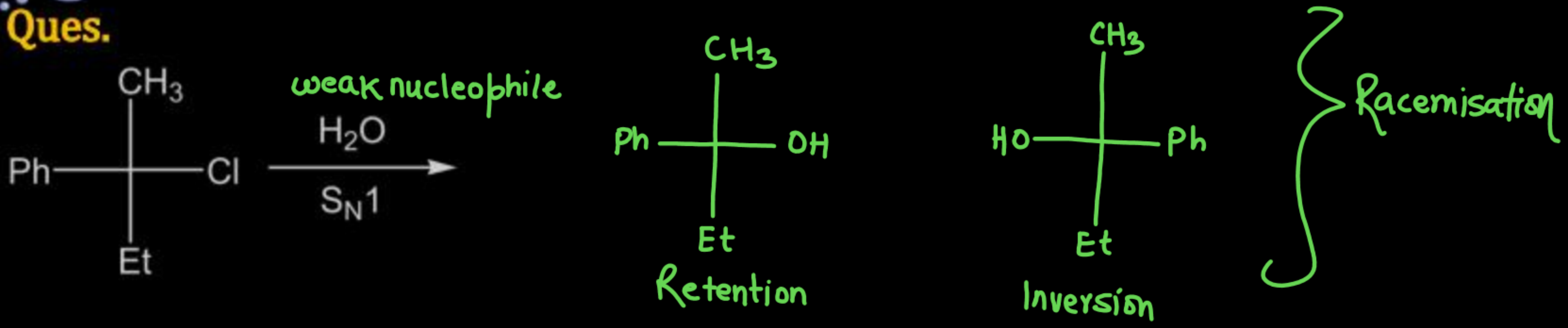
Ques.


weak nucleophile
H_2O
S_N1
Cl
OH
OH

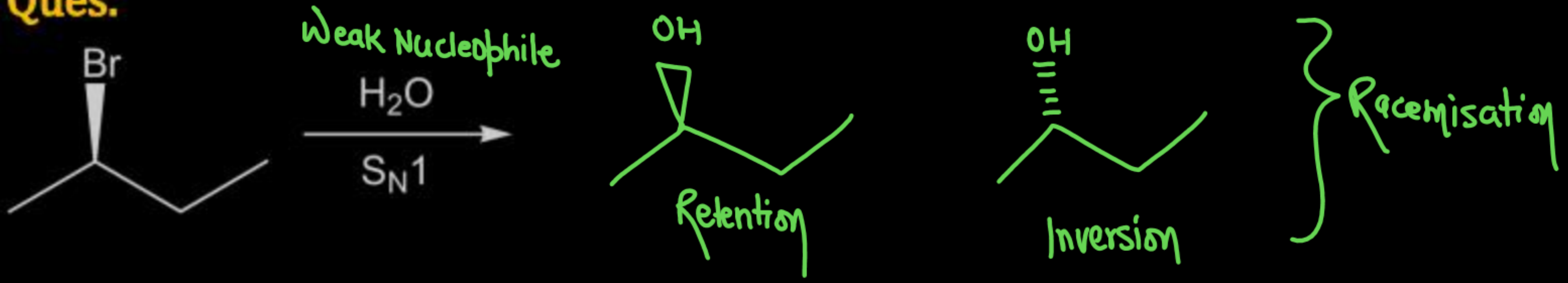
Ques.


CH_3
Ph—CH—C—Br
CH_3 CH_3
weak nucleophile
R—OH
S_N1
Ph—CH—C—OR
CH_3
CH_3 CH_3
Ph—CH—C—OR
CH_3
CH_3 CH_3

Ques.


CH3
Ph
Cl
Et
weak nucleophile
H2O
SN1
CH3
Ph
OH
Et
Retention
CH3
HO
Ph
Et
Inversion
Racemisation

Ques.


Br
Weak Nucleophile
H2O
SN1
OH
Retention
OH
Inversion
Racemisation

N.A.S.

Identify reaction and compare their rate:

Ques.1

$1°$ R–X

(a) $HS^{\ominus} + H_3C - Cl \xrightarrow{DMSO}$ Strong Nu^- (SN^2) CH_3-SH

(b) $HS^{\ominus} + H_3C - Cl \xrightarrow{H_2O}$ Strong Nu^- (SN^2) CH_3-SH

Rate → a > b

Ques.

(a) $H_3C - O^{\ominus} + H_3C - Cl \xrightarrow{DMSO}$ SN^2 CH_3-O-CH_3

(b) $Ph - O^{\ominus} + H_3C - Cl \xrightarrow{DMSO}$ SN^2 CH_3-O-Ph

Rate → a > b

Strong Nu → $CH_3-O^- > Ph-O^-$

Ques.

(a) $HS^{\ominus} + H_3C - Cl \xrightarrow{\text{DMSO}}$

(b) $HO^{\ominus} + H_3C - Cl \xrightarrow{\text{DMSO}}$

Ques.

(a) $HS^{\ominus} + H_3C - Cl \xrightarrow{H_2O}$

(b) $HO^{\ominus} + H_3C - Cl \xrightarrow{H_2O}$

NAS

Ques.

(a) $H_3\underline{C}^{\ominus} + H_3C - Cl \xrightarrow{DMSO}$ $CH_3 - CH_3$

(b) $\overset{\ominus}{\underline{N}}H_2 + H_3C - Cl \xrightarrow{DMSO}$ $CH_3 - NH_2$

Rate → a > b

Ques.

(a) $H_3C - CH_2 - Cl \xrightarrow{NaSH}$ S_N1 $CH_3 - CH_2 - SH$

(b) $H_3C - \underset{\substack{|\\CH_3}}{CH} - Cl \xrightarrow{NaSH}$ S_N1 $CH_3 - \underset{\substack{|\\CH_3}}{CH} - SH$

Rate → b > a

Rate of Reaction → R−I > R−Br > R−Cl > R−F

Ques.

1° alkyl Halide

(a) $H_3C-CH_2-Br \xrightarrow{\ddot{N}H_3} CH_3-CH_2-NH_2$ SN1

(b) $H_3C-CH_2-I \xrightarrow{\ddot{N}H_3} CH_3-CH_2-NH_2$ SN1

1° alkyl Halide

Rate → b > a

Ques.

(a) $R-\underset{R}{\overset{H}{C}}-I \xrightarrow{H_2O}$ SN1 $\quad R-\underset{R}{\overset{H}{C}}-OH$

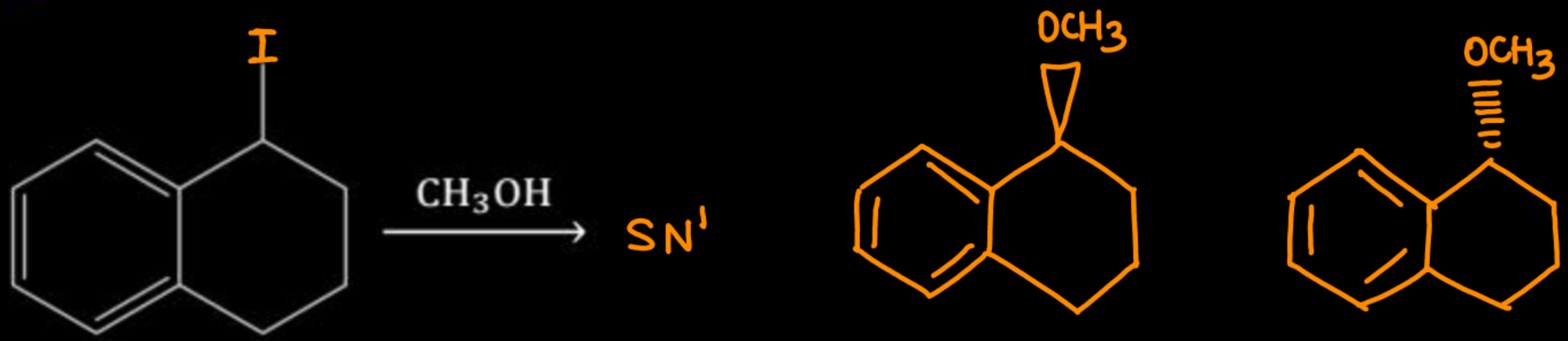
(b) $R-\underset{R}{\overset{H}{C}}-Br \xrightarrow{H_2O}$ SN1 $\quad R-\underset{R}{\overset{H}{C}}-OH$

Rate → a > b

~~NAS~~

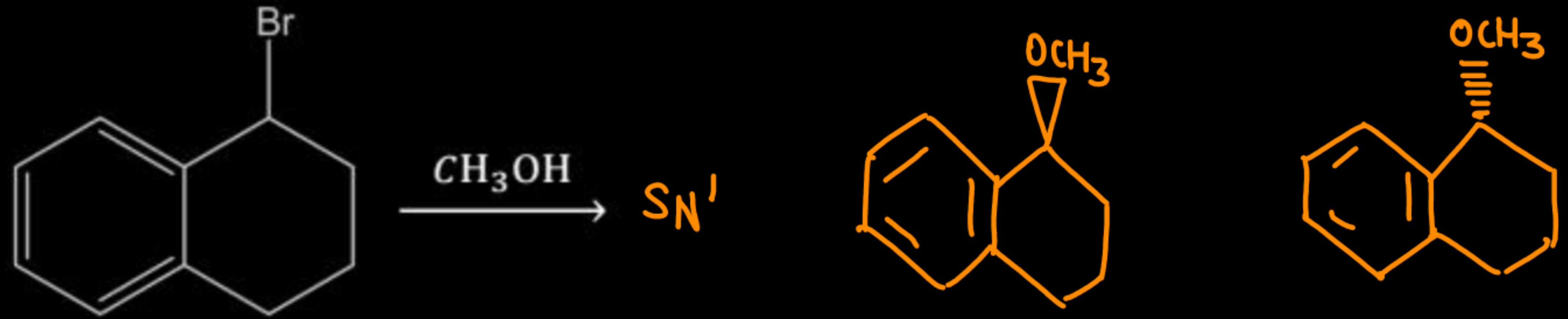
Ques.

(a)



Racemisation

(b)



Racemisation

Rate → a > b



Ques. (imp)

H_2O ↑ moisture ↑

(a) $2\,R - Cl \xrightarrow[\text{AgOH}]{\text{(Moist } Ag_2O\text{) or}}$ S_N1 $2R-OH$ alcohol

Nucleophile = H_2O

(b) $\overset{\delta+}{2\,R} - \overset{\delta-}{Cl} \xrightarrow{\text{Dry } Ag_2O}$ $R-\ddot{O}-Ag$; $\overset{\delta+}{R}-Cl$ → $R-O-R$ ether

Nucleophile = Ag_2O



SN^1

- Order = 1
- Molecularity = 1
- Unimolecular Reaction
- Rate ∝ [R–X]
- Weak Nucleophile
- Solvent acts as nucleophile.
- Two step Rxn
  - Step 1 → Carbocation Formation.
  - Step 2 → Nucleophile attack.
- Retention as well as Inversion both products are formed.
- Rate of SN^1 → $3^\circ RX > 2^\circ RX > 1^\circ RX$
- Rate of SN^1 ∝ Stab of Carbocation
- polar protic Solvent

SN^2

Order = 2

Molecularity = 2

Bimolecular Reaction

Rate ∝ [R–X] [Nu^-]

Strong Nucleophile

Nucleophile is taken अलग से

one step Rxn

No intermediate is formed.

- Walden inversion/Umbrella inversion.
- only inversion product is product.

Rate of SN^2 → $1^\circ RX > 2^\circ RX > 3^\circ RX$

Rate of SN^2 ∝ $\frac{1}{\text{steric crowding}}$

- polar aprotic solvent.

Elimination Reaction

Haloalkane having atleast one β–H on Simple heating removes Small molecule like HX is known as elimination Reaction. (α,β elimination)

$$\overset{}{CH_3}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-Cl \xrightarrow[-HX]{\Delta} CH_3-CH=CH_2 + HCl$$

Haloalkane → alkene

Two types of elimination Reaction -

(i) E^1 Reaction

(ii) E^2 Reaction



E^1 Reaction

- order = 1.
- Unimolecular Reaction.
- Rate ∝ [R — X]
- 2 step Rxn
  1. Carbocation Formation.
  2. Removal of β Hydrogen to form alkene.

Step 1: $CH_3-\overset{\beta}{CH}(H)-\overset{\alpha}{CH_2}(X) \longrightarrow CH_3-CH(H)-\overset{\oplus}{CH_2}$

Step 2: $CH_3-CH(H)-\overset{\oplus}{CH_2} \longrightarrow CH_3-CH=CH_2$

- Intermediate → Carbocation
- Rate → 3° R–X > 2° R–X > 1° R–X
- Rate → RI > RBr > RCl > RF

Temp ≤ 25°c	SN^1
Temp ≥ 50°c	E^1

at Temp b/w 25°c – 50°c both SN^1 & E^1 Can occur.

- Polar protic solvent is used.
- More stable alkene → Major product } Saytzeff Rule / Saytzeff Product / Saytzeff alkene
  Less Stable alkene → Minor product } Hoffman Rule / Hoffman product / Hoffman alkene
- Heat is required in this rxn.

Compare rate of E_1 reaction:

Ques



a>b>c

Ques.



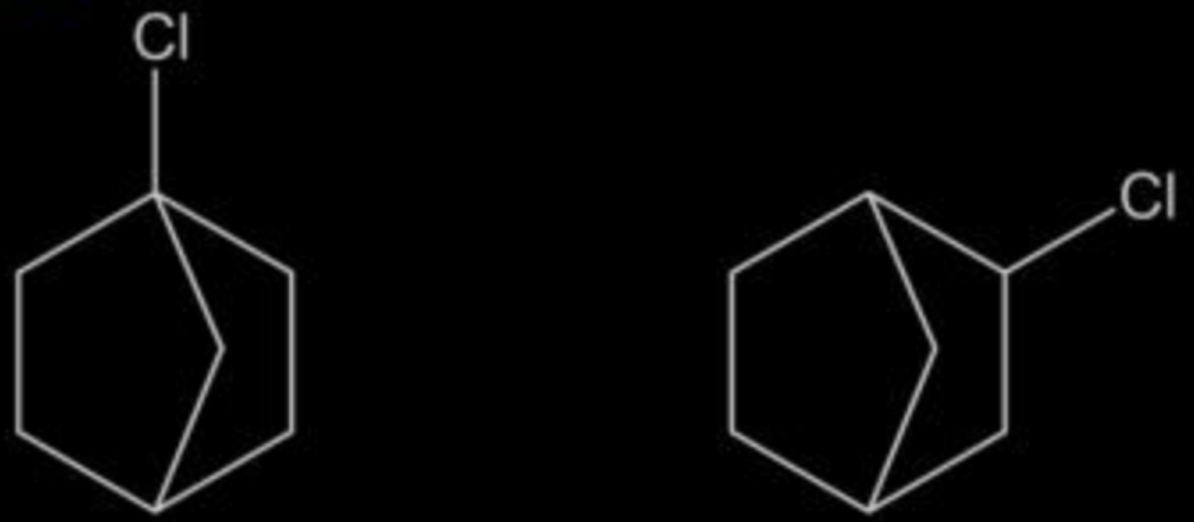
a>b

Ques.



a>b>c>d

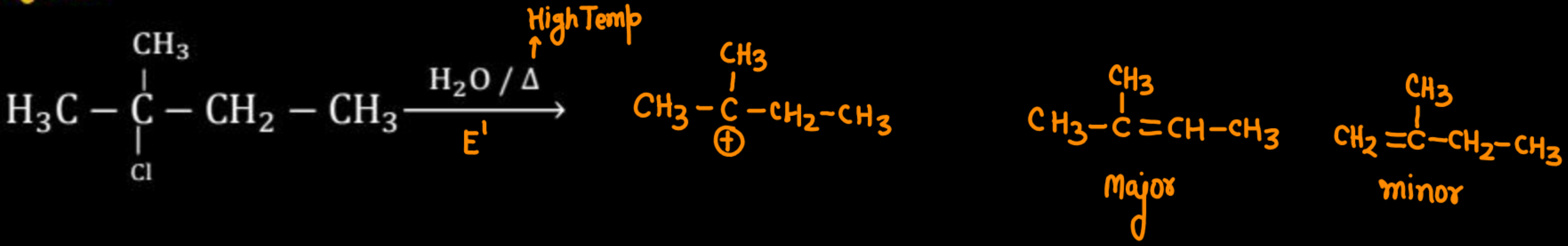
Ques.



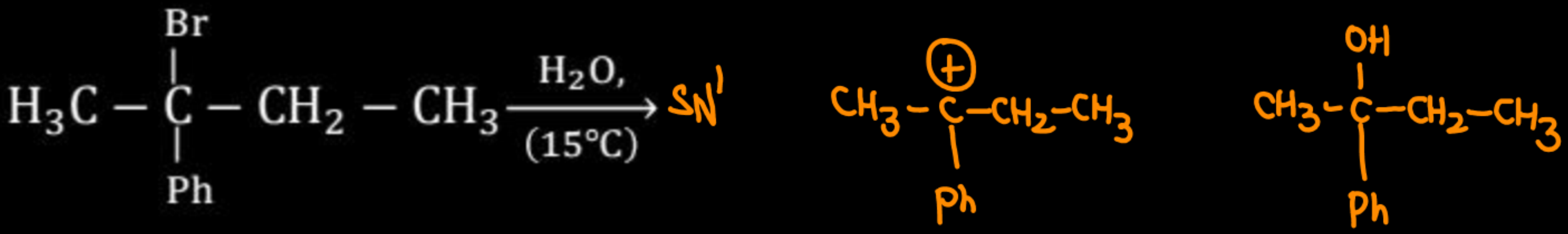
b>a

Identify the product:

Ques.



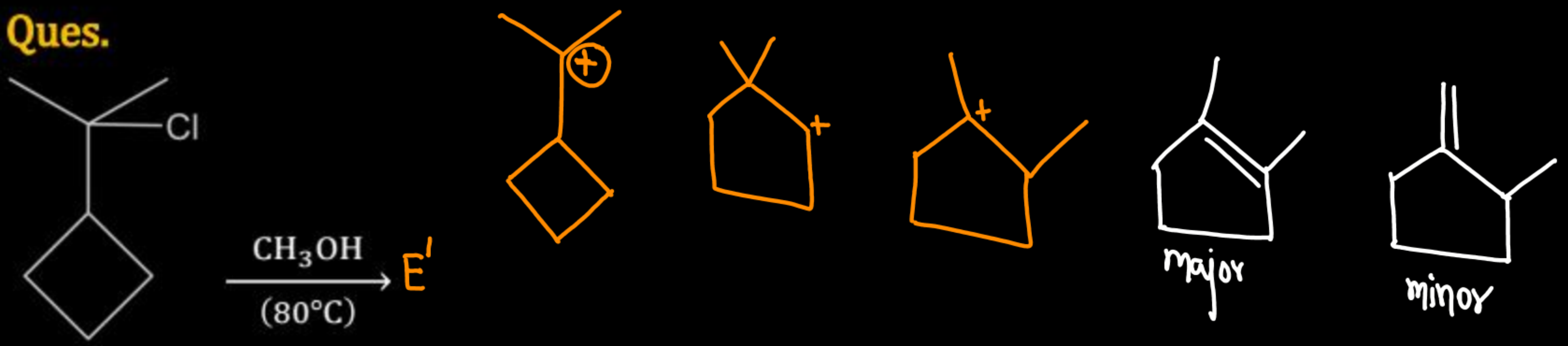
Ques.



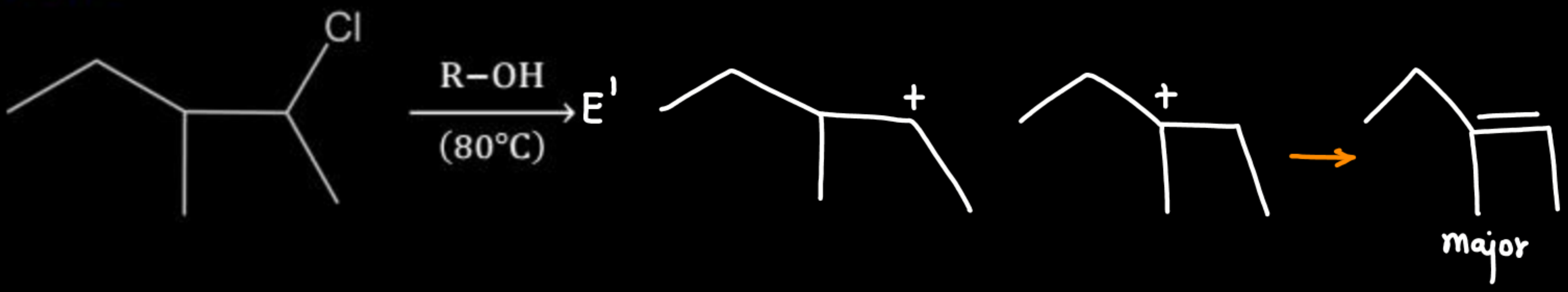
Ques.

$$H_3C-\underset{Ph}{\overset{Br}{C}}-CH_2-CH_3 \xrightarrow[\text{high temp. (80°C)}]{H_2O,} CH_3-\underset{Ph}{\overset{\oplus}{C}}-CH_2-CH_3 \qquad \underset{\text{Major}}{CH_3-\underset{Ph}{C}=CH-CH_3} \qquad \underset{\text{Minor}}{CH_2=\underset{Ph}{C}-CH_2-CH_3}$$

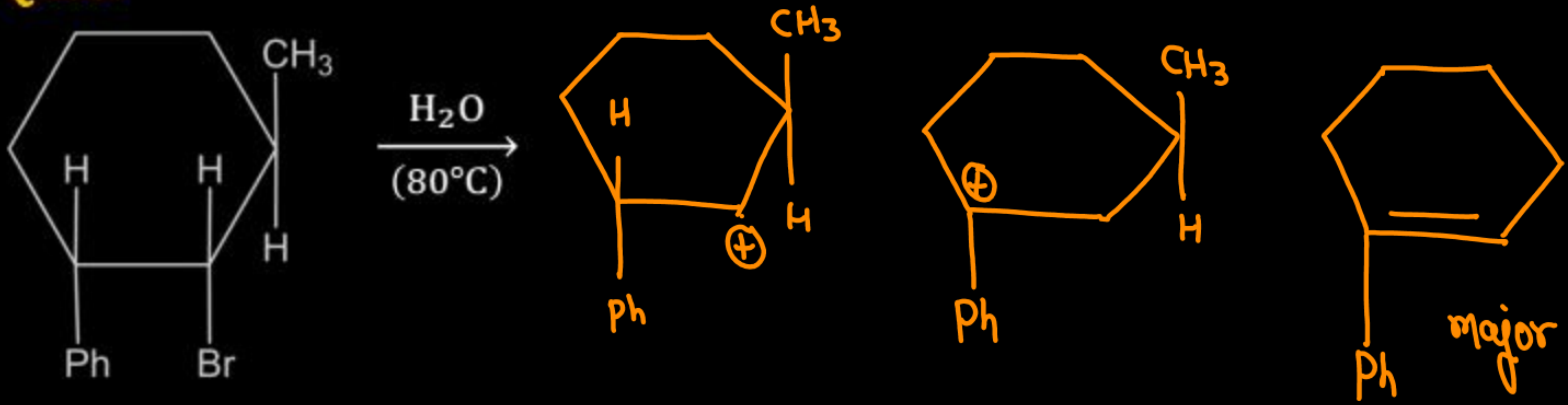
Ques.



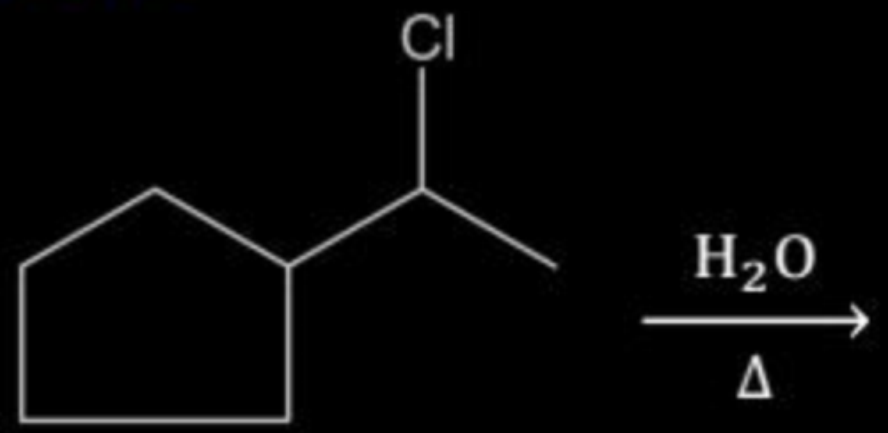
Ques.



Ques.



Ques.



Ques.

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \xrightarrow[(100^\circ C)]{R-OH}$$

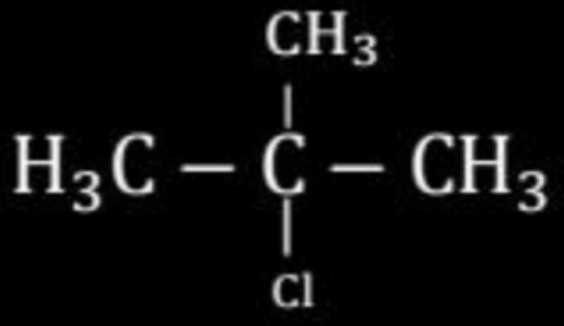
E^2 Reaction

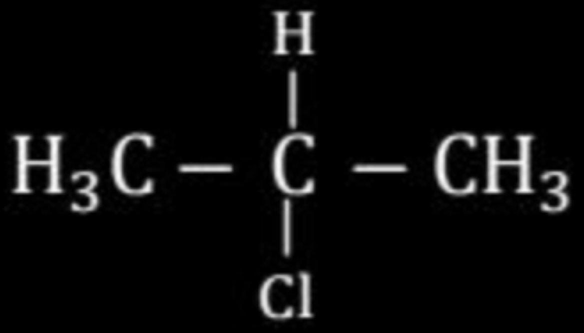
- Order = 2
- Bimolecular Reaction
- Rate $\propto [R-X][Nu^-]$
- One step Rx^n
- Strong Nucleophile
- $CH_3-CH(H)-CH_2(Cl) \xrightarrow[\Delta]{alc\,KOH} CH_3-CH=CH_2$
- Polar aprotic Solvent.
- No Intermediate form.
- High Temp
- Strong base alc KOH/Δ
  alc NaOH/Δ
  $NaNH_2/\Delta$
   O^-/Δ → Tertiarybutoxide is a bulky base & forms Hoffmann alkene.(major)
  $R-O^-/\Delta$

Rate of $E^2 \propto$ Stability of alkene

Compare rate of E_2 reaction:

Ques.

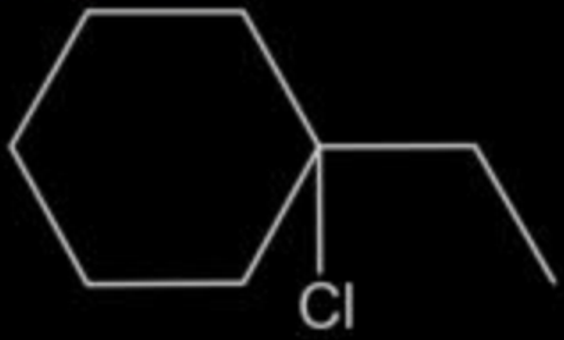


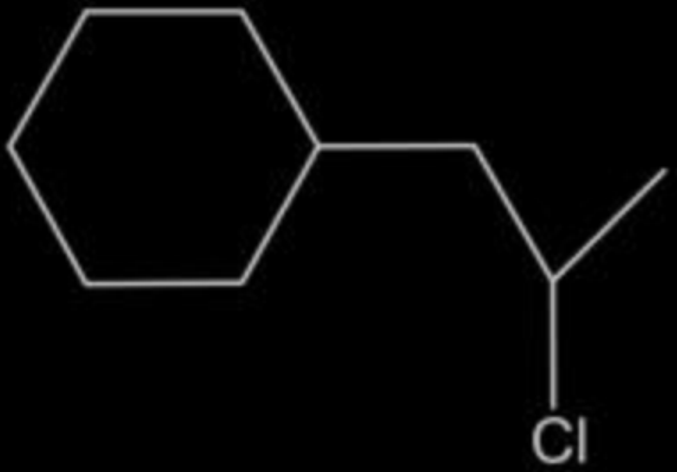


$H_3C - CH_2 - Cl$

a > b > c

Ques.

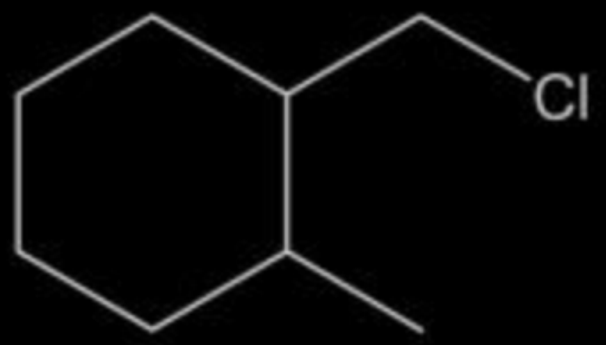




a > b

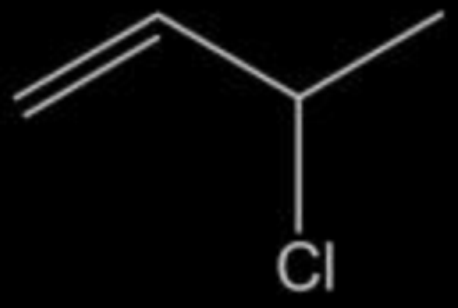
Ques.





a > b

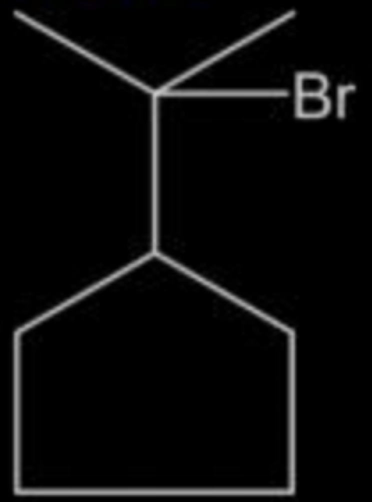
Ques.

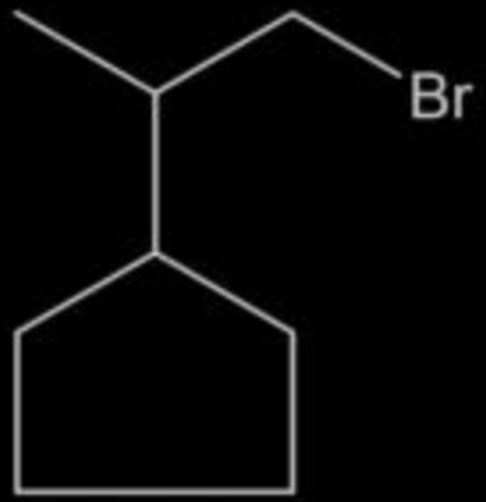




a > b

Ques.

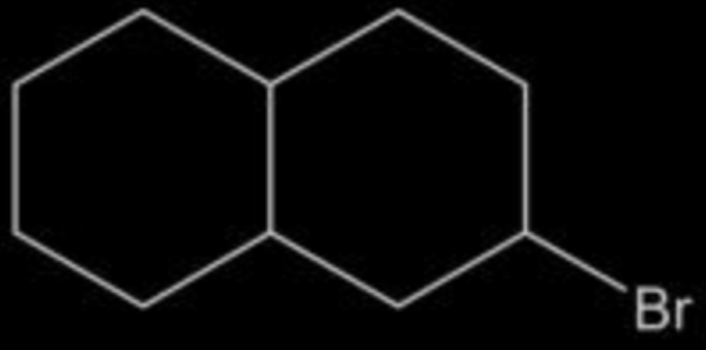




a>b

Ques.





a>b

SN^1	SN^2	E^1	E^2
Rate ∝ Stab of Carbocation	Rate ∝ $\frac{1}{\text{Steric crowding}}$	Rate ∝ Stab of Carbocation	Rate ∝ Stab of alkene
$T \leq 25^\circ c$		$T \geq 50^\circ c$	
Polar protic Solvent	polar aprotic Solvent	polar protic solvent	Strong base
			alc KOH/Δ
			alc NaOH/Δ
			$NaNH_2$/Δ
			RO^-/Δ

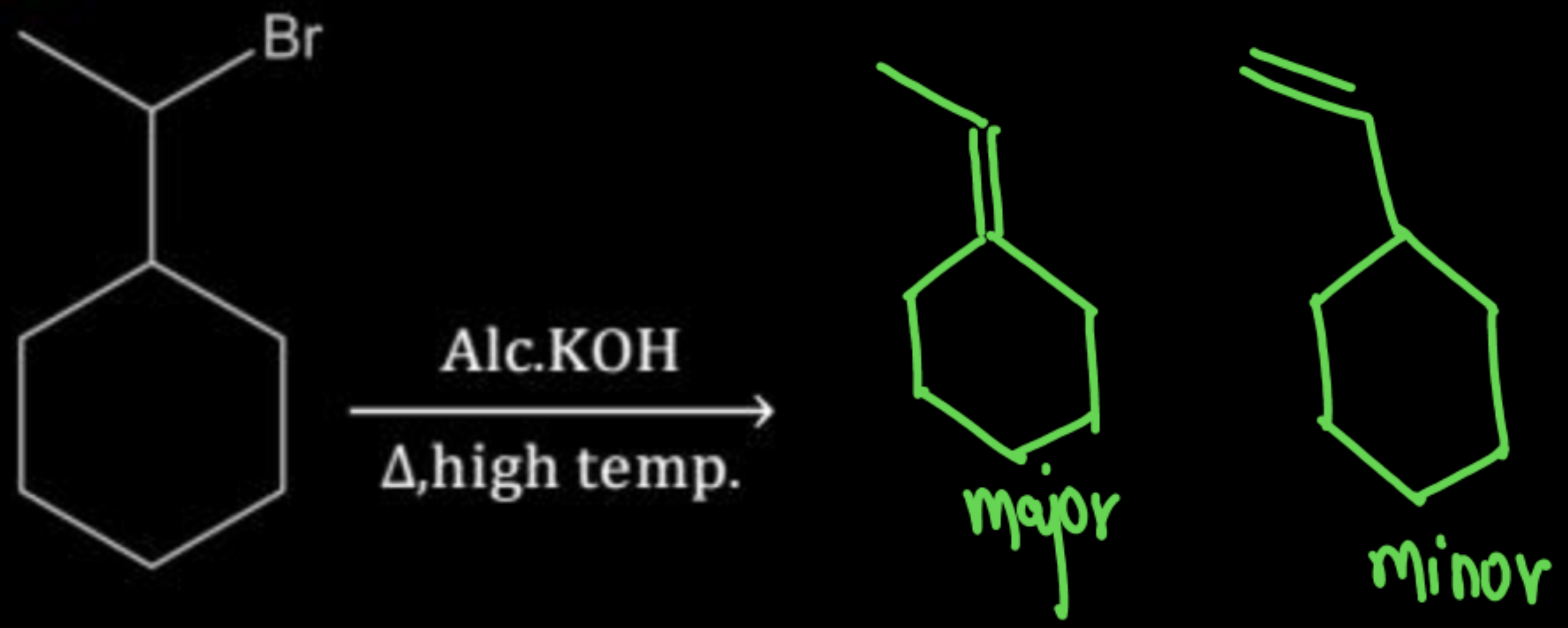
Identify the product:

Ques.

$$H_3C-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3 \xrightarrow[CH_3OH/\Delta]{CH_3ONa} E^2 \quad CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3 \quad H_2C=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3$$

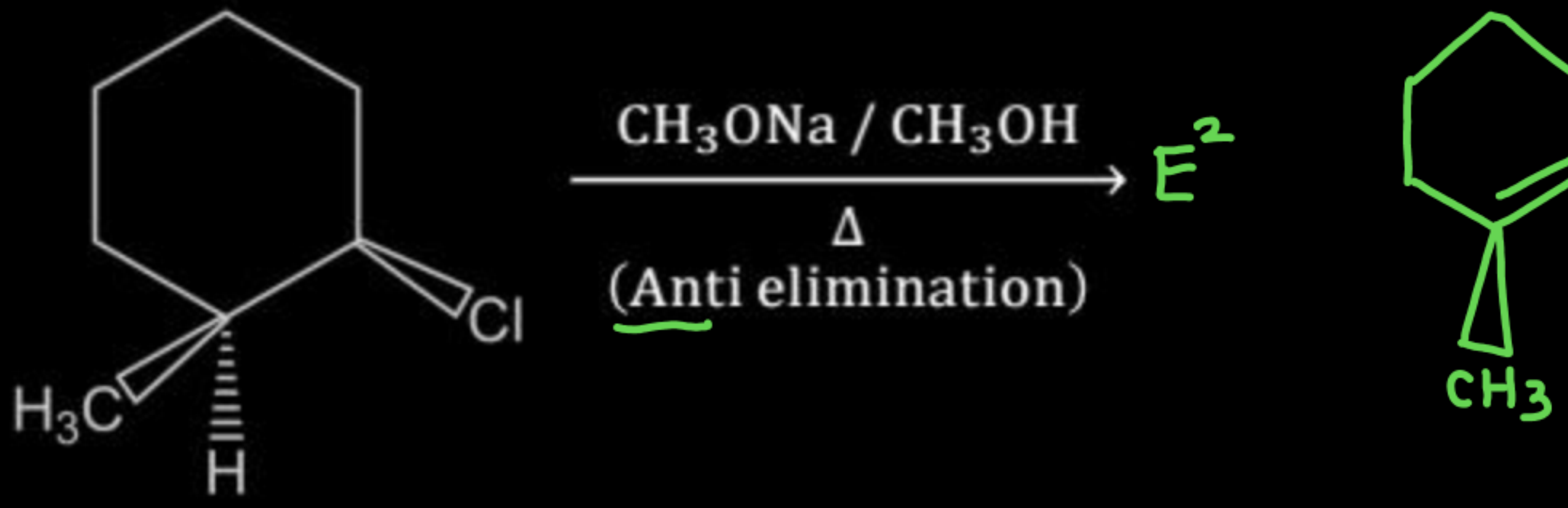
Major   Minor

Ques.

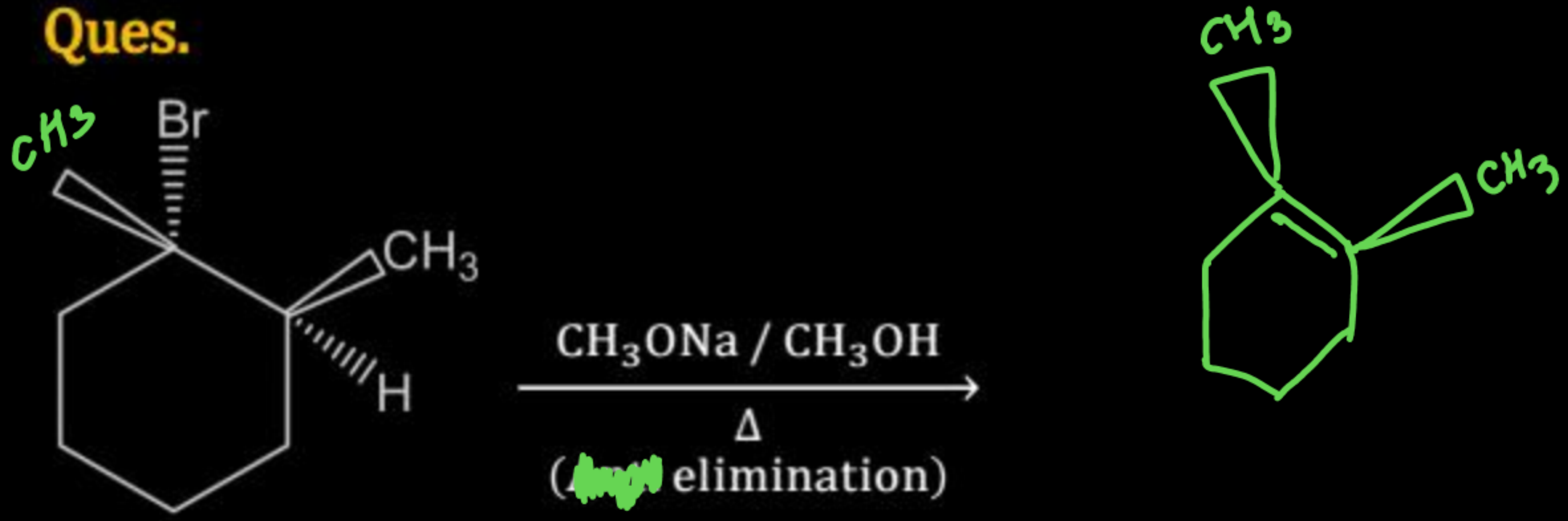


Identify the product:

Ques.



Ques.



Ques.

$$H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br \xrightarrow[100^\circ C]{H_2O}$$

E^1

$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$$

Ques.

$$H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br \xrightarrow[15^\circ C]{H_2O}$$

SN^1

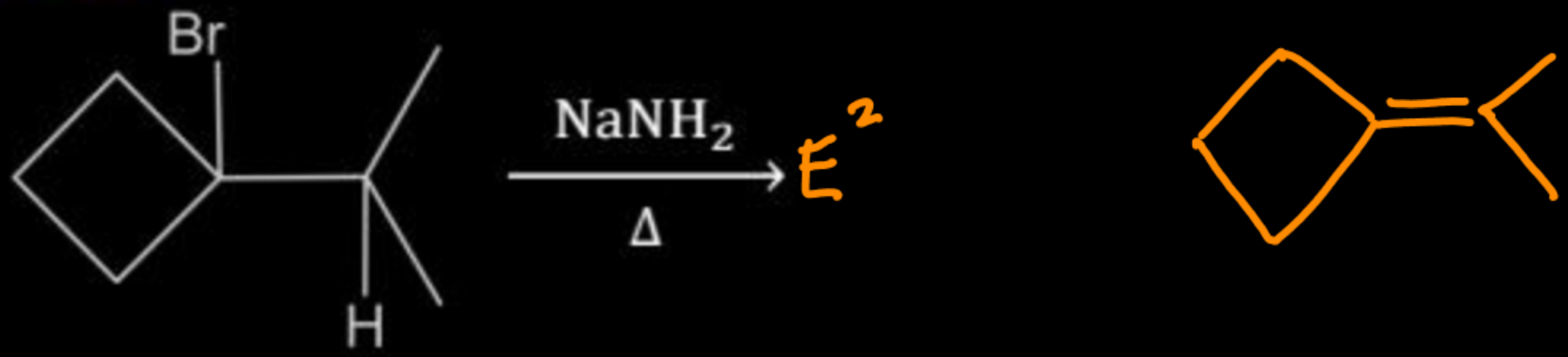
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

Ques.

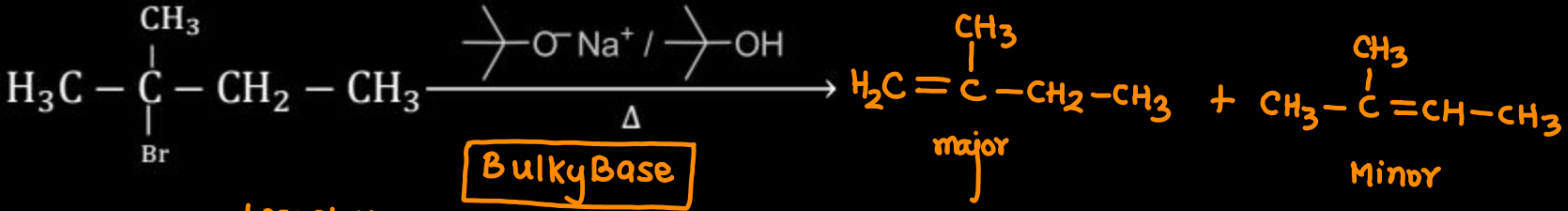
$$H_3C-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-Br \xrightarrow[\Delta(E_2)]{alc.KOH} E^2$$

$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$$

Ques.



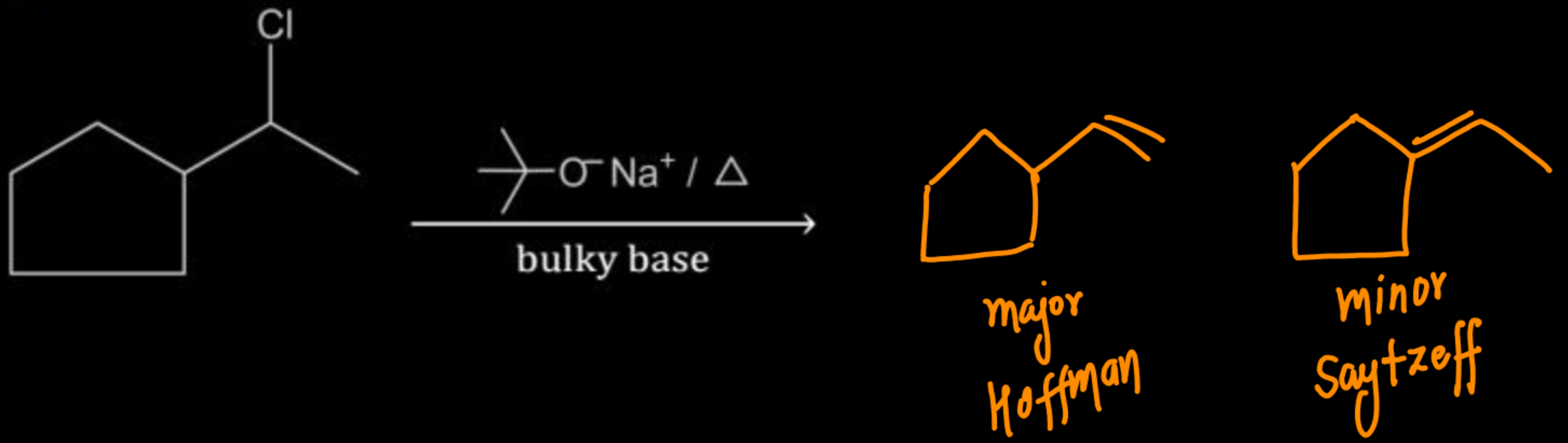
Ques.



Less stable alkene → Hoffman alkene → major

More stable alkene ↗ Saytzeff alkene → minor

Ques.



Ques.



Saytzeff alkene
Major

Hoffman alkene
Minor



Comparison of S_N1 S_N2 E_1 E_2

Alkyl Halide	Mechanism	Solvent	Temp	nucleophile
1° Alkyl Halide	SN^2	Polar aprotic	Low	Strong
	E^2	Polar aprotic	High	Strong
2° Alkyl Halide	SN^1	polar protic	Low	weak
	E^1	Polar protic	High	weak
	SN^2	polar aprotic	Low	strong
	E^2	polar aprotic	High	strong
3° Alkyl Halide	SN^1	polar protic	Low	weak
	E^1	Polar protic	High	Weak
	E^2	polar aprotic	High	Strong

moderate nucleophile

aq NaOH
aq KOH
NaSH
NaI

} gives SN^2 with 1° & 2° alkyl Halide

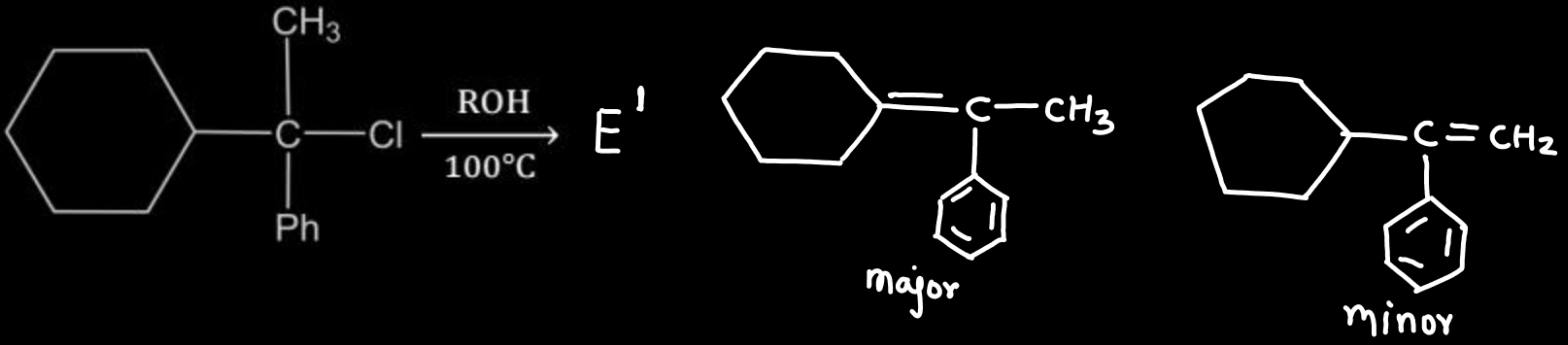
Strong nucleophile

⇒ alc KOH/Δ
alc NaOH/Δ
CH_3-O^-/Δ
$C_2H_5-O^-/\Delta$
$NaNH_2/\Delta$
 O^-/Δ

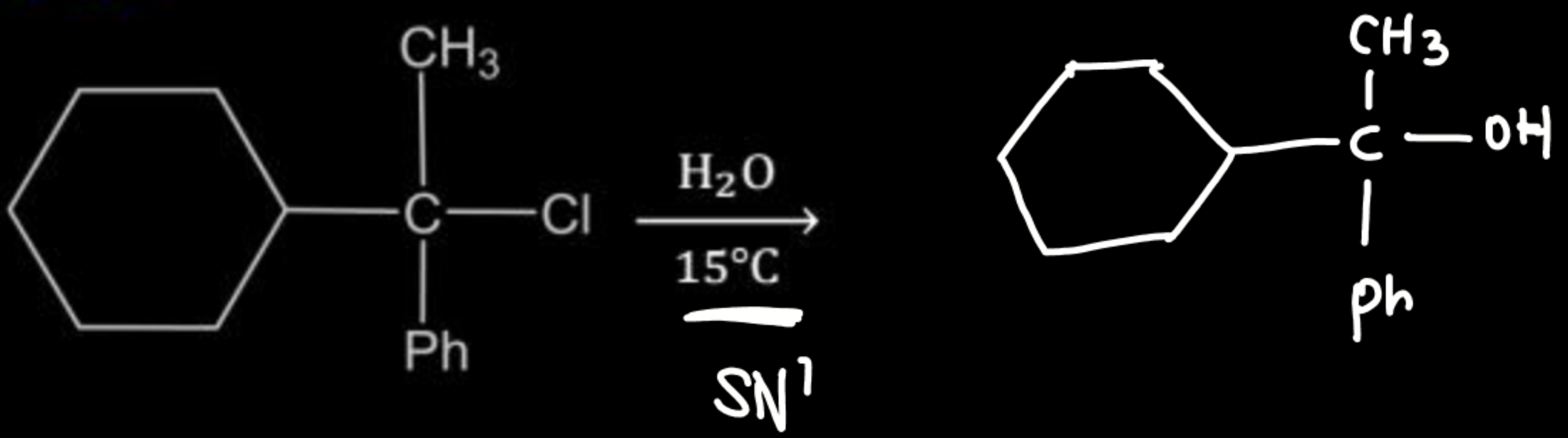
Weak nucleophile

H_2O
CH_3OH
PhOH
RCOOH

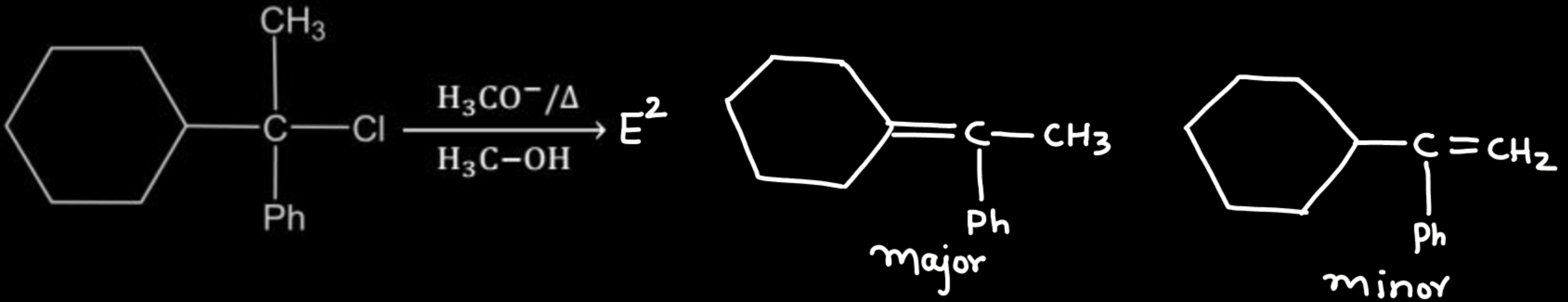
Ques.


CH3
C
Cl
Ph
ROH
100°C
E1
C
CH3
major
C
CH2
minor

Ques.

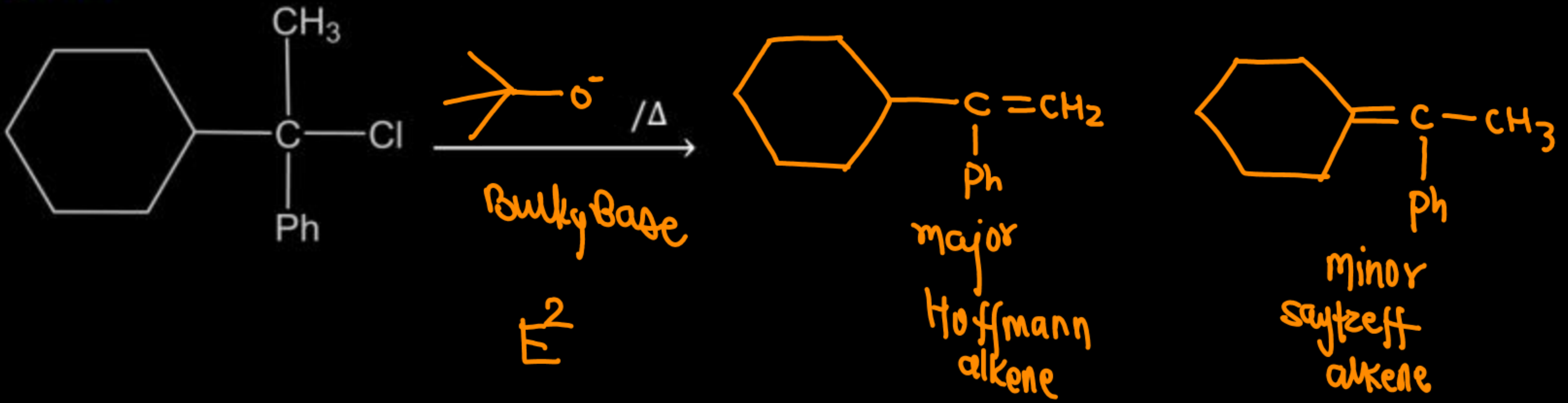

CH3
C
Cl
Ph
H2O
15°C
SN1
CH3
C
OH
ph

Ques.



CH3
C
Cl
Ph
H3CO⁻/Δ
H3C–OH
E2
C
CH3
Ph
major
C
CH2
Ph
minor

Ques.



CH3
C
Cl
Ph
O⁻
/Δ
Bulky Base
E2
C
CH2
Ph
major
Hoffmann alkene
C
CH3
Ph
minor
saytzeff alkene

Identify A and B in the product:

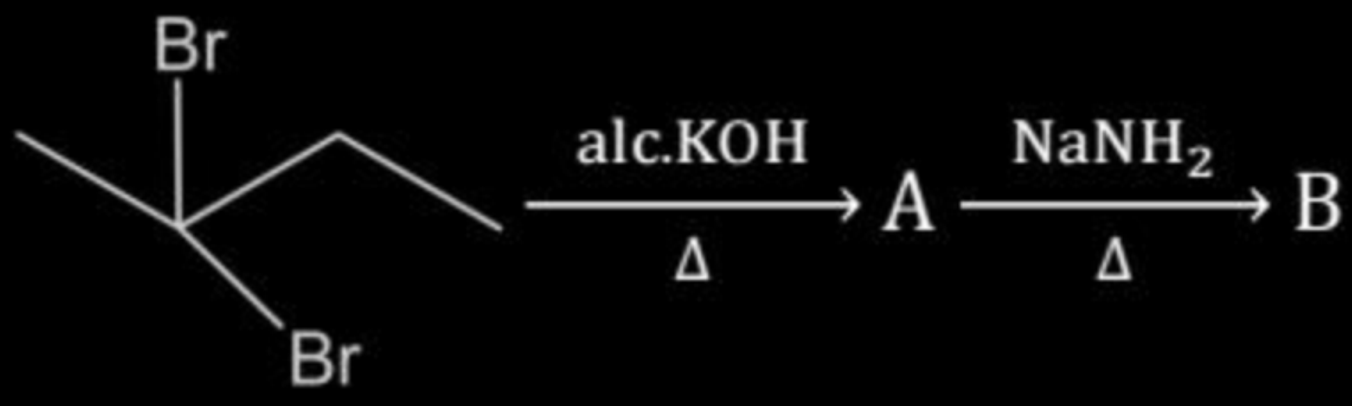
Ques.

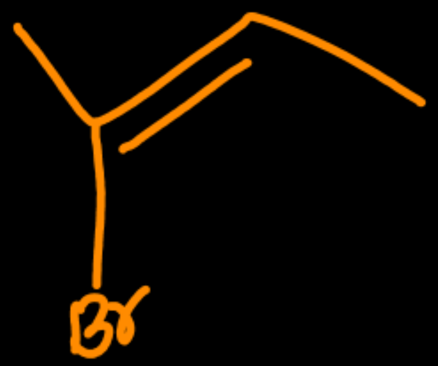
$$H_3C-\underset{Cl}{\overset{Cl}{C}}-CH_3 \xrightarrow[\Delta]{\text{alc.KOH}\ (E^2)} A \xrightarrow[\Delta]{NaNH_2\ (E^2)} B$$

$A = CH_2=\underset{Cl}{C}-CH_3$ $B = CH\equiv C-CH_3$

Resonance

Ques.





(A)



(B)

Identify the reaction (S_N1, S_N2, E_1, E_2) & find product:

Ques.

$$H_3C - CH_2 - Cl \xrightarrow[\text{moderate nucleophile}]{\text{Aq.KOH}}$$ (SN^2) $CH_3 - CH_2 - OH$

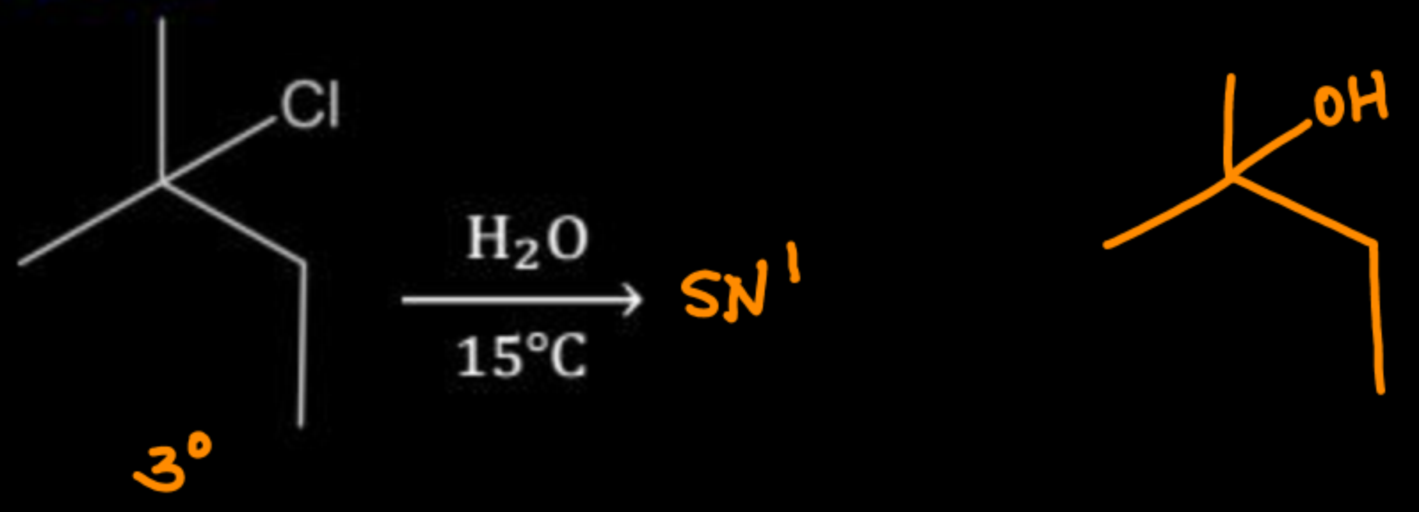
$1°$

Ques.

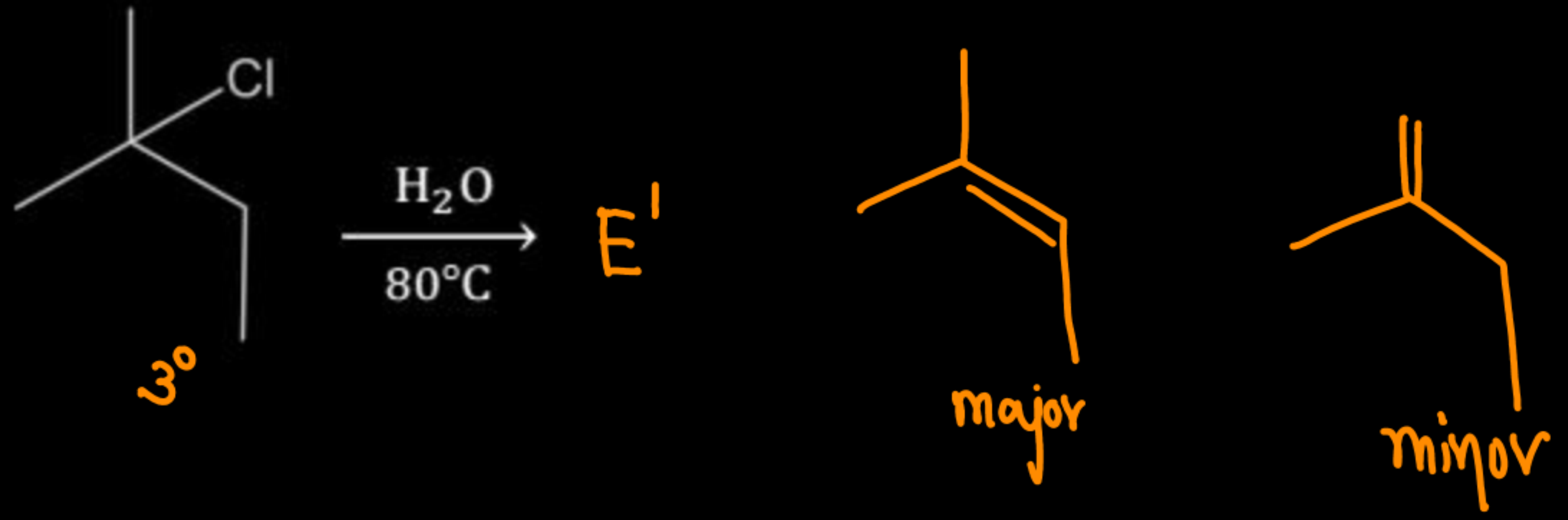
$$H_3C - CH_2 - Cl \xrightarrow[\text{Strong nucleophile}]{\text{Alc.KOH}/\Delta}$$ (E^2) $CH_2 = CH_2$

$1°$

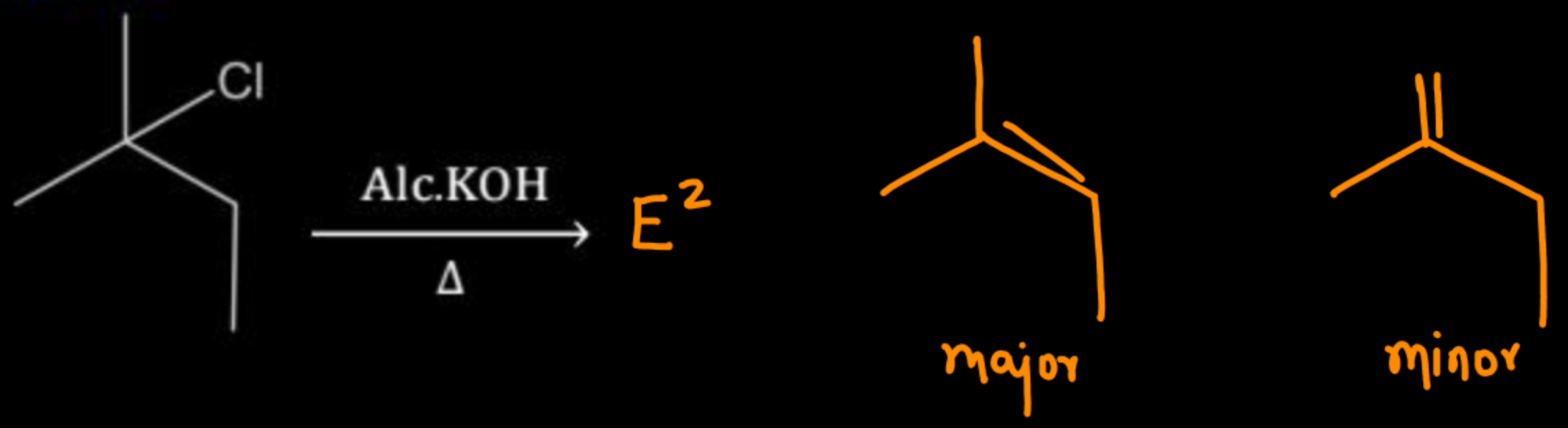
Ques.



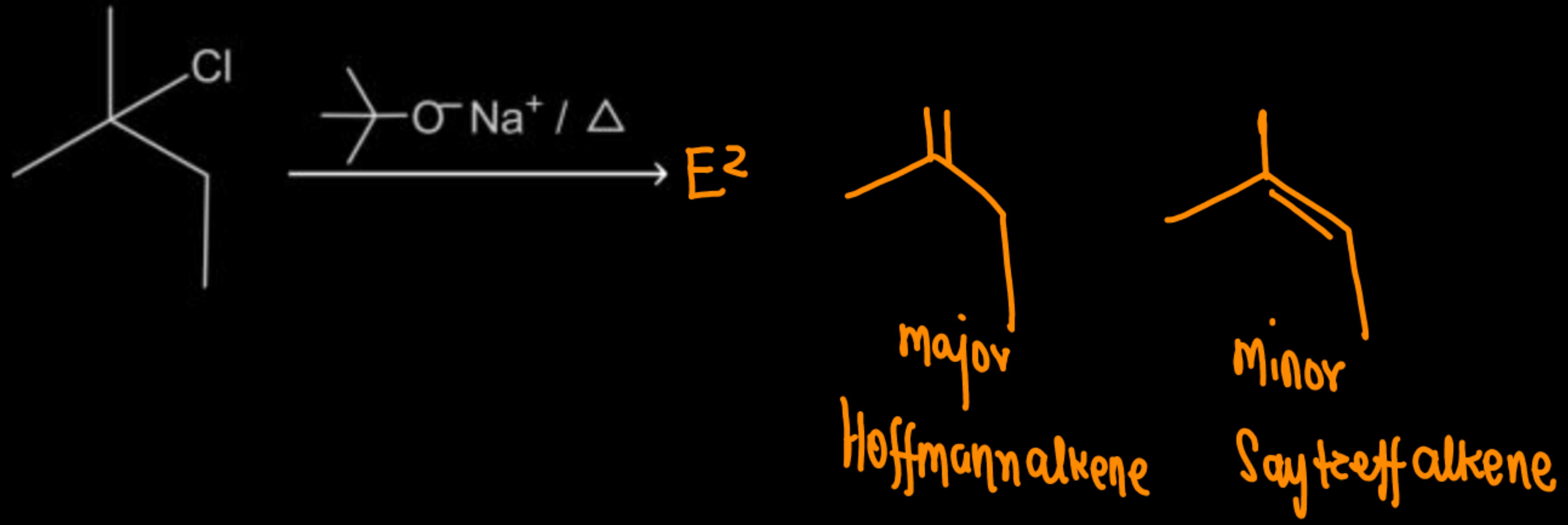
Ques.



Ques.


Cl
Alc.KOH
Δ
E2
major
minor

Ques.


Cl
O⁻ Na⁺ / Δ
E2
major
Hoffmann alkene
minor
Saytzeff alkene

Ques.

$$Ph-\underset{\substack{|\\Br}}{CH}-CH_3 \xrightarrow[\Delta]{Alc.KOH} E^2 \qquad Ph-CH=CH_2$$

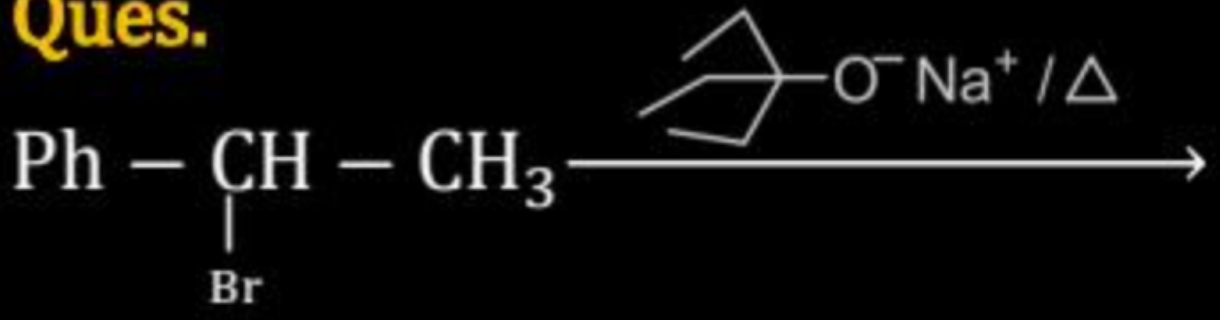
Ques.

$CH_3-COO^-\ H^+$

$$Ph-\underset{\substack{|\\Br}}{CH}-CH_3 \xrightarrow[10^\circ C]{H_3C-COOH} \qquad Ph-\underset{\substack{|\\OOC-CH_3}}{CH}-CH_3$$

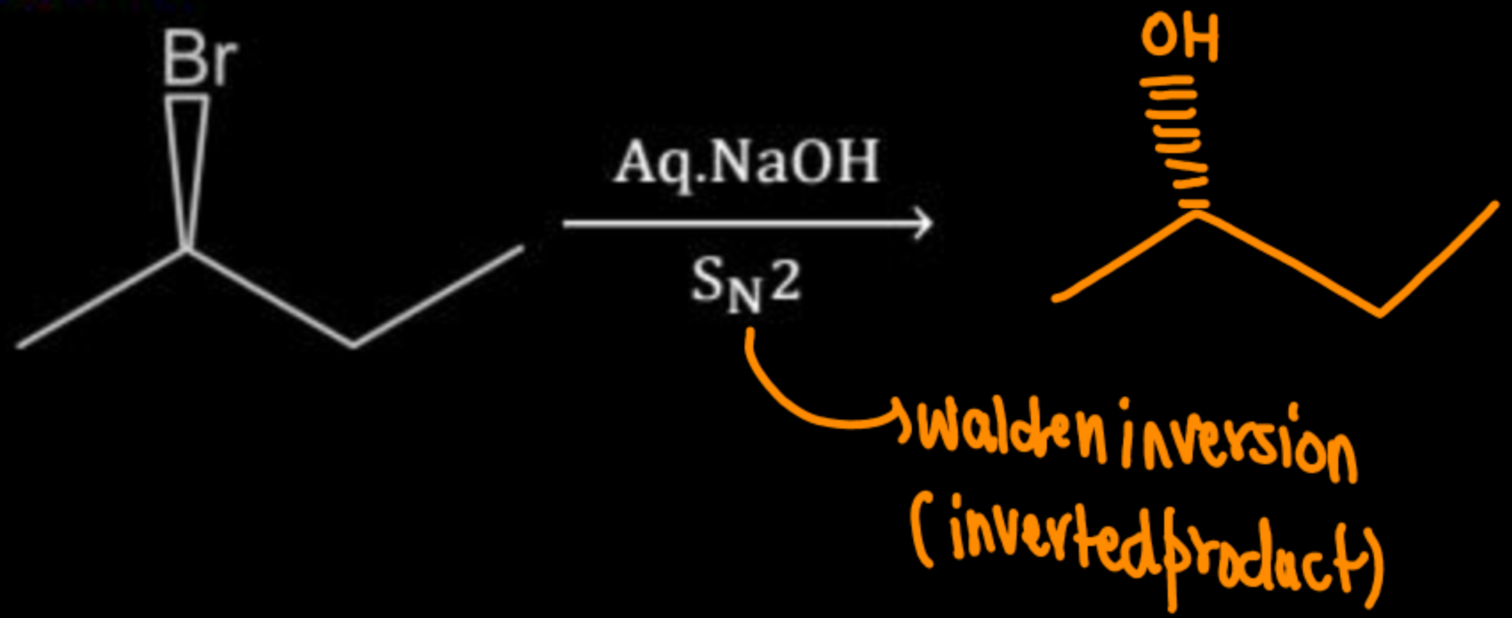
SN^1

Ques.

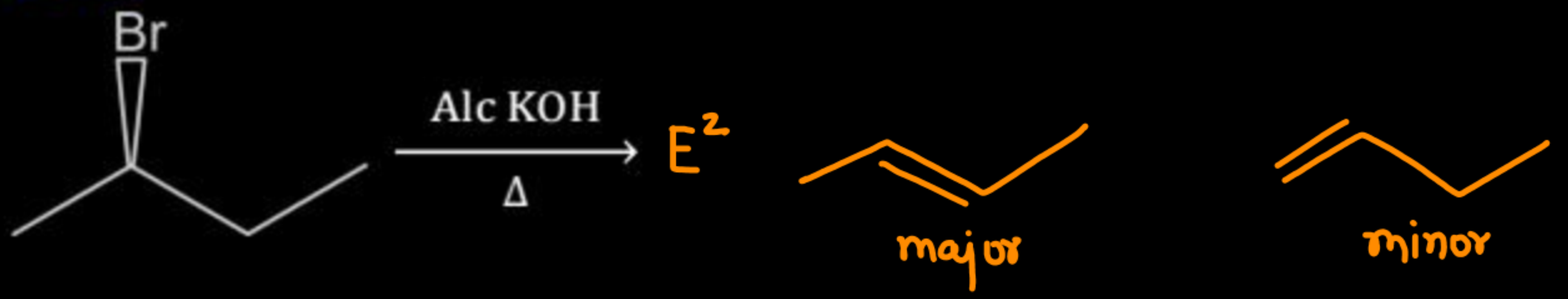


$Ph-CH=CH_2$ (Single product)

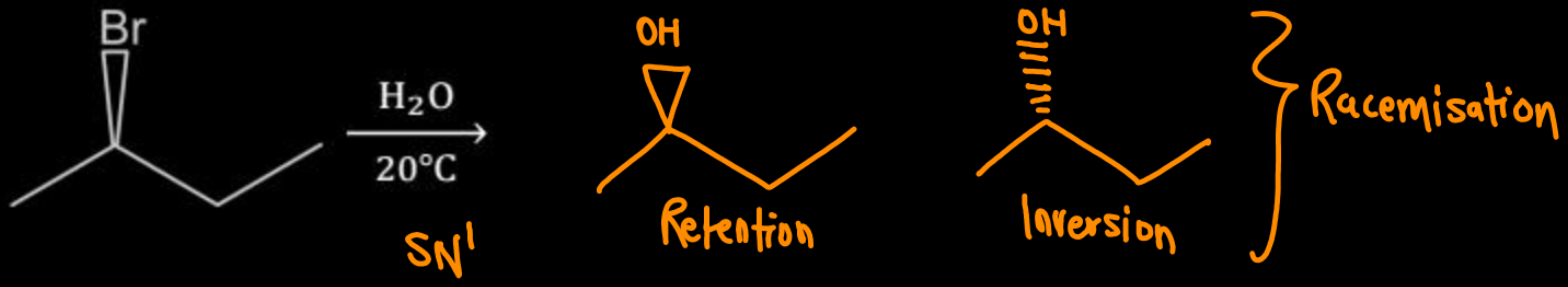
Ques.



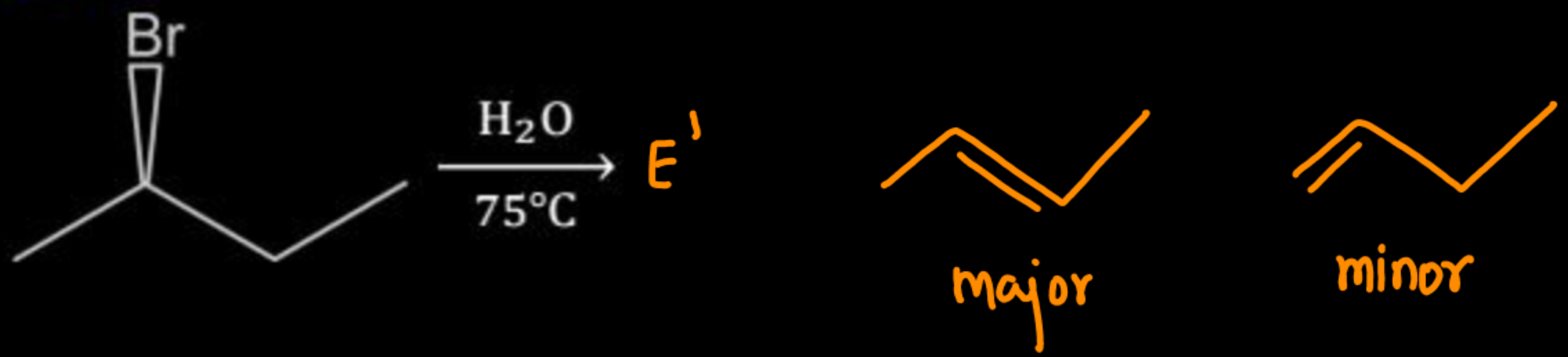
Ques.


Br
Alc KOH
Δ
E2
major
minor

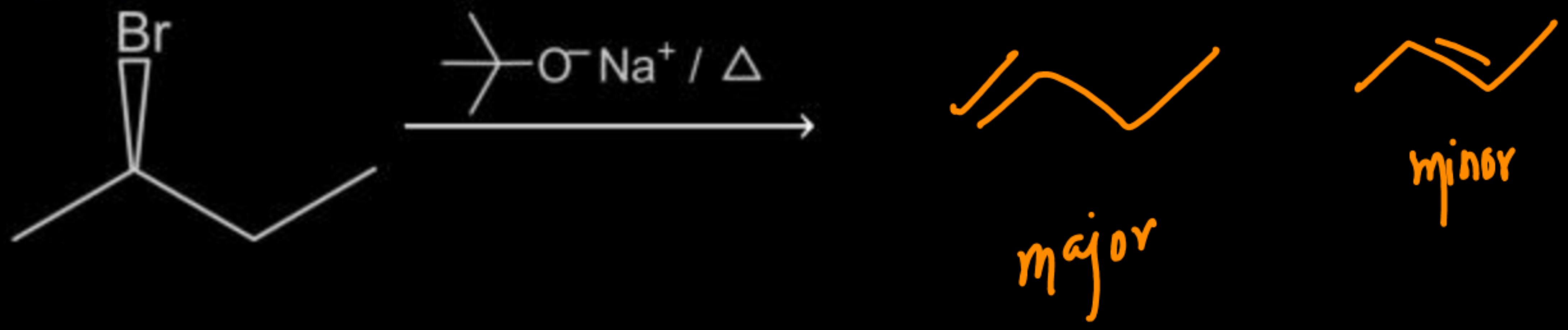
Ques.


Br
H2O
20°C
SN1
OH
OH
Retention
Inversion
Racemisation

Ques.



Ques.



Ques.

$$Ph - CH_2 - Cl \xrightarrow{Aq.NaOH}$$

Ques.

$$Ph - CH_2 - Cl \xrightarrow{ROH}$$

Ques.

$$H_2C = CH - CH_2 - Cl \xrightarrow{H_2O}$$

Ques.

$$H_2C = CH - CH_2 - Cl \xrightarrow{Aq.NaOH}$$

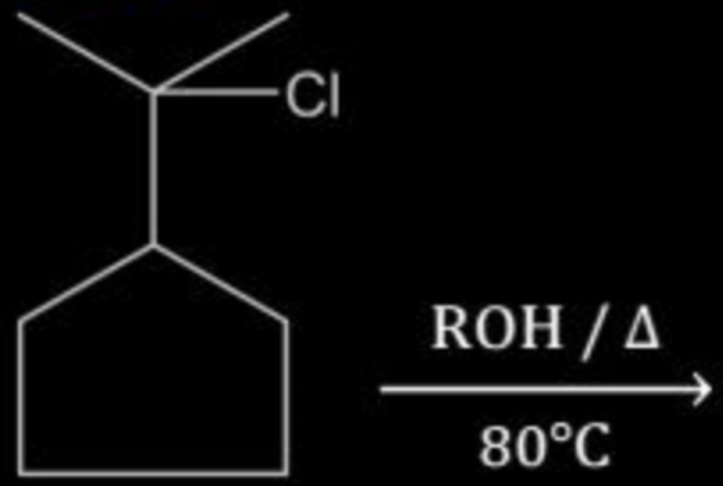
Ques.

$$H_2C = CH - Cl \xrightarrow{\text{Aq.KOH}}$$

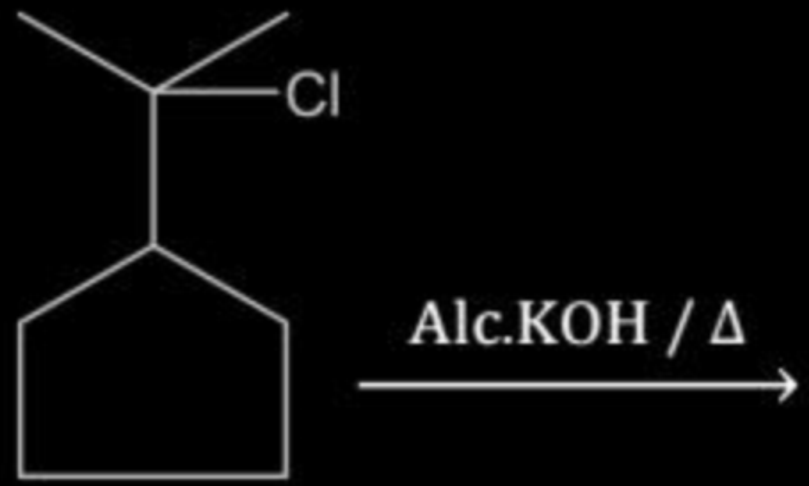
Ques.

$$H_2C = CH - Cl \xrightarrow{NaNH_2\ /\ \Delta}$$

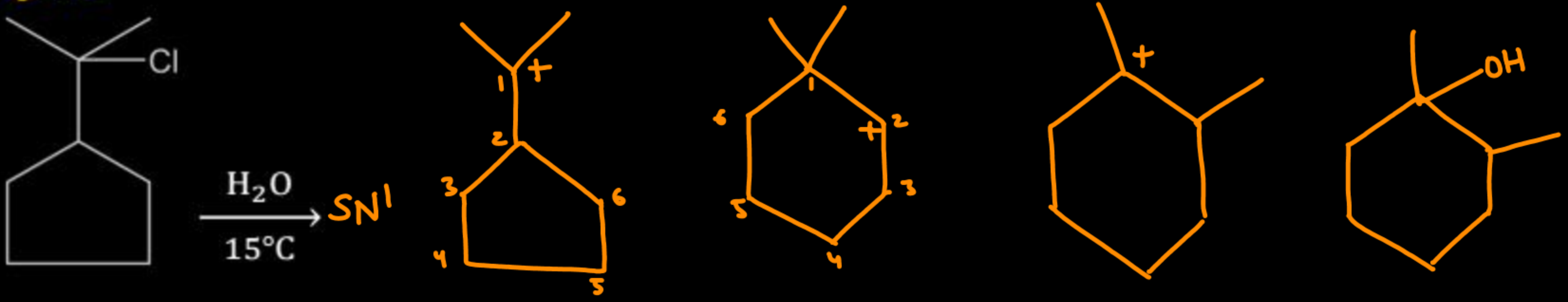
Ques.



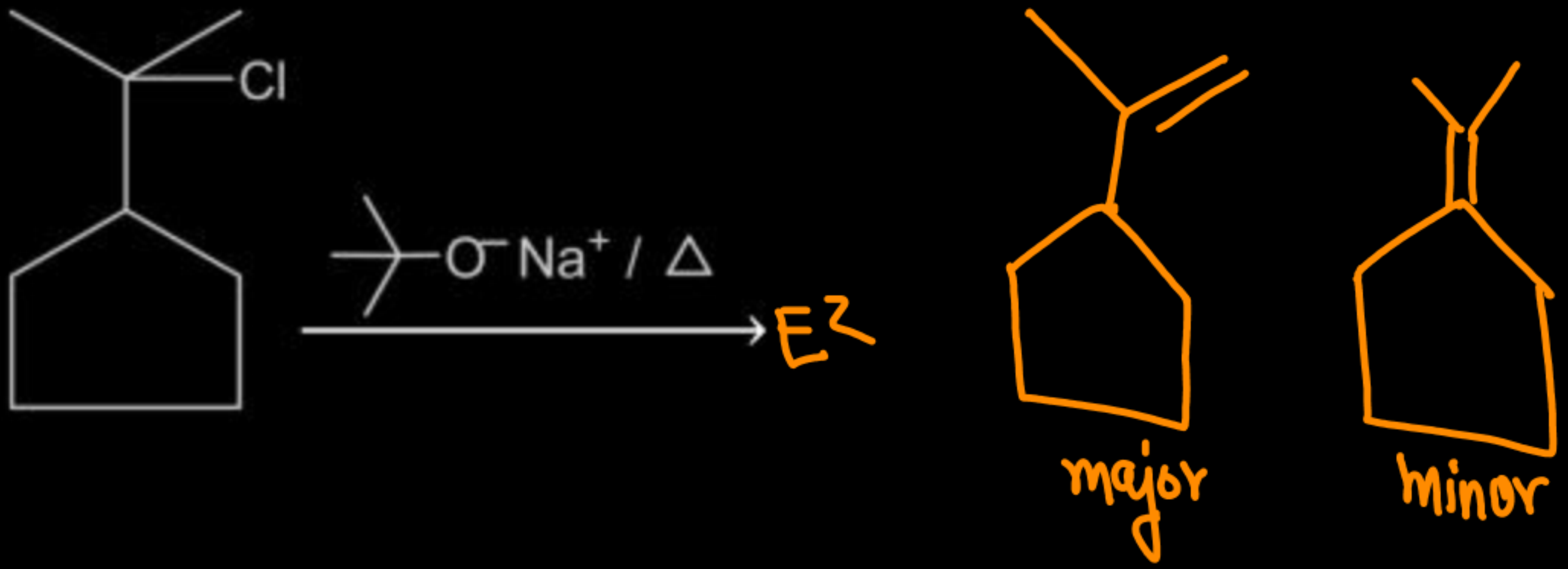
Ques.



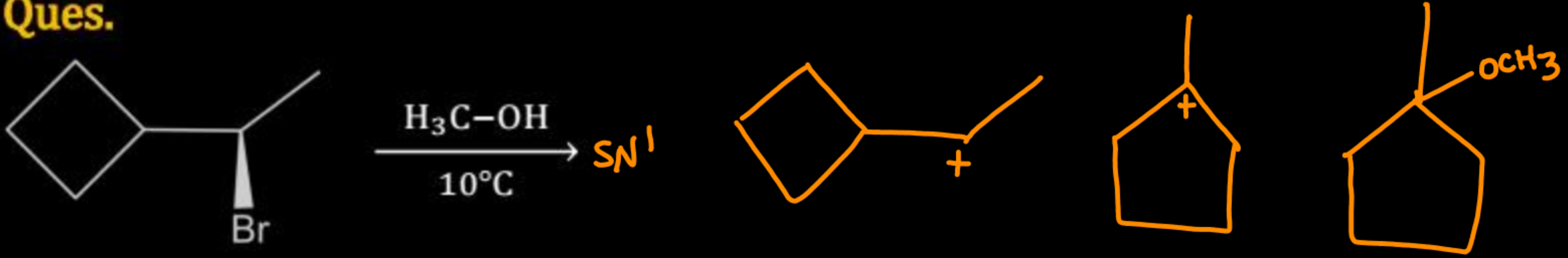
Ques.



Ques.



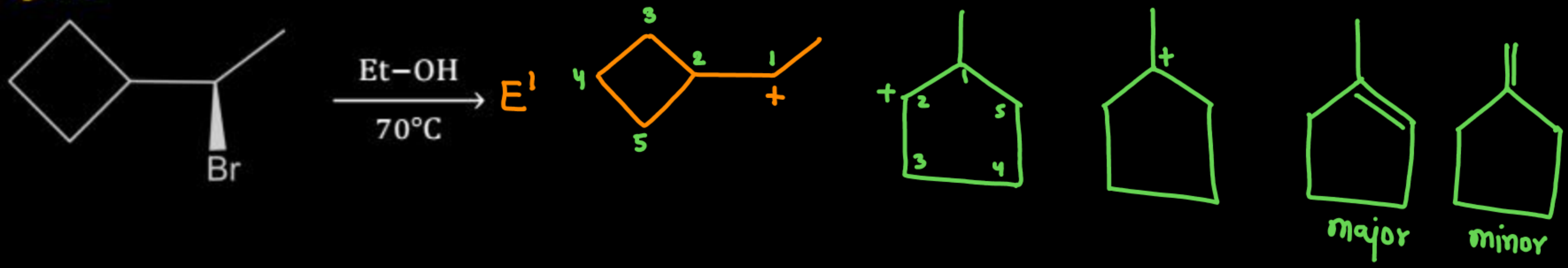
Ques.



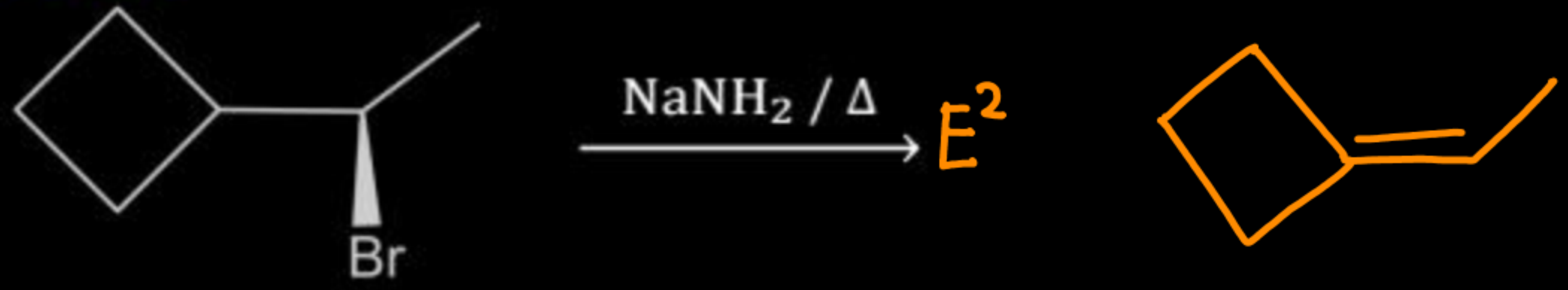
Ques.



Ques.



Ques.





Williamson Ether Synthesis → S_N2

1° alkyl Halide reacts with alkoxide ion to form ether is k/a williamson ether synthesis.

william का son की 1^{st} GF Alkyl Halide, alkoxide के साथ भाग गई और ether बना लिया ।

$$CH_3-CH_2-Cl + \overset{-}{O}-R \longrightarrow CH_3-CH_2-O-R$$

} This is a S_N2 Reaction.

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-Cl + {}^{-}O-R \longrightarrow \times$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl + {}^{-}O-R \longrightarrow \times$$

$$CH_3-CH_2-Cl + {}^{-}O-CH_3 \longrightarrow CH_3-CH_2-O-CH_3$$

$$+ {}^{-}O-CH(CH_3)_2 \longrightarrow CH_3-CH_2-O-CH(CH_3)_2$$

$$+ {}^{-}O-C(CH_3)_3 \longrightarrow CH_3-CH_2-O-C(CH_3)_3$$

$$Ph-CH_2-Cl + CH_3-CH_2-O^- \longrightarrow Ph-CH_2-O-CH_2-CH_3$$

$$Ph-CH(CH_3)-Cl + CH_3-CH_2-O^- \longrightarrow \times$$

$$(CH_3)_3C-O^- + CH_3-Cl \longrightarrow (CH_3)_3C-O-CH_3$$

Reaction with Metal

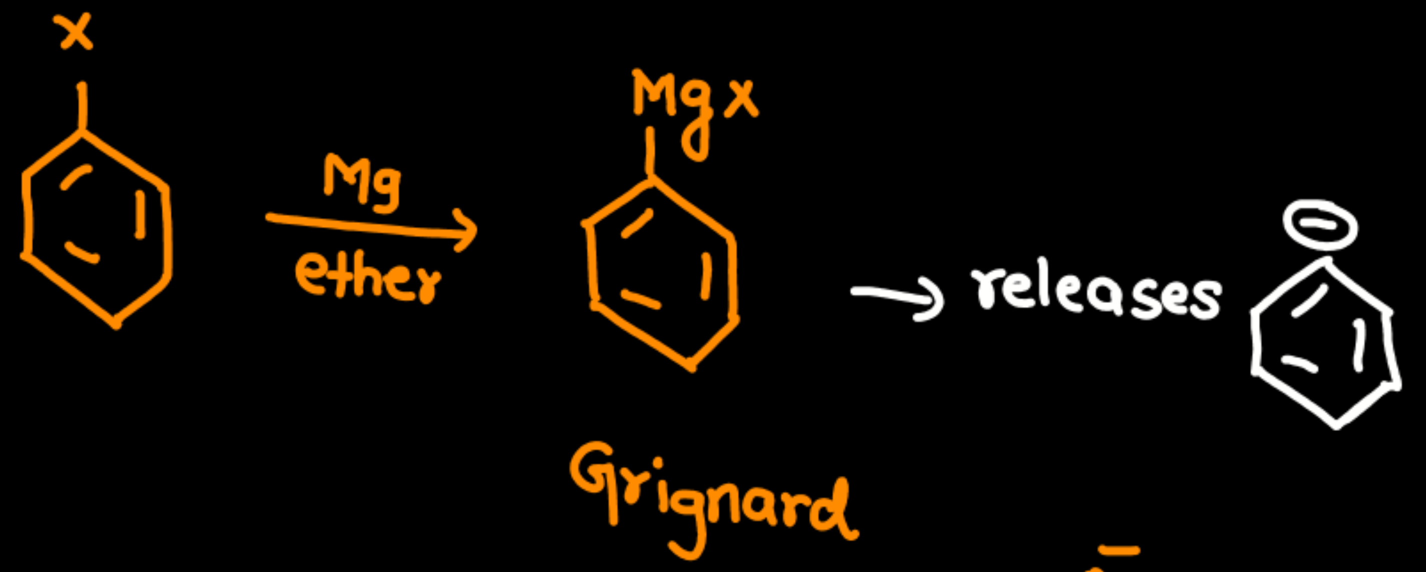
1. Grignard Reagent
2. Wurtz Reaction PPCH
3. Frankland Reaction PPCH
4. Corey House Synthesis PPCH
5. Friedal craft Reaction PPCH
6. Alkyl Halide $\xrightarrow{\text{reduction}}$ Alkane PPCH

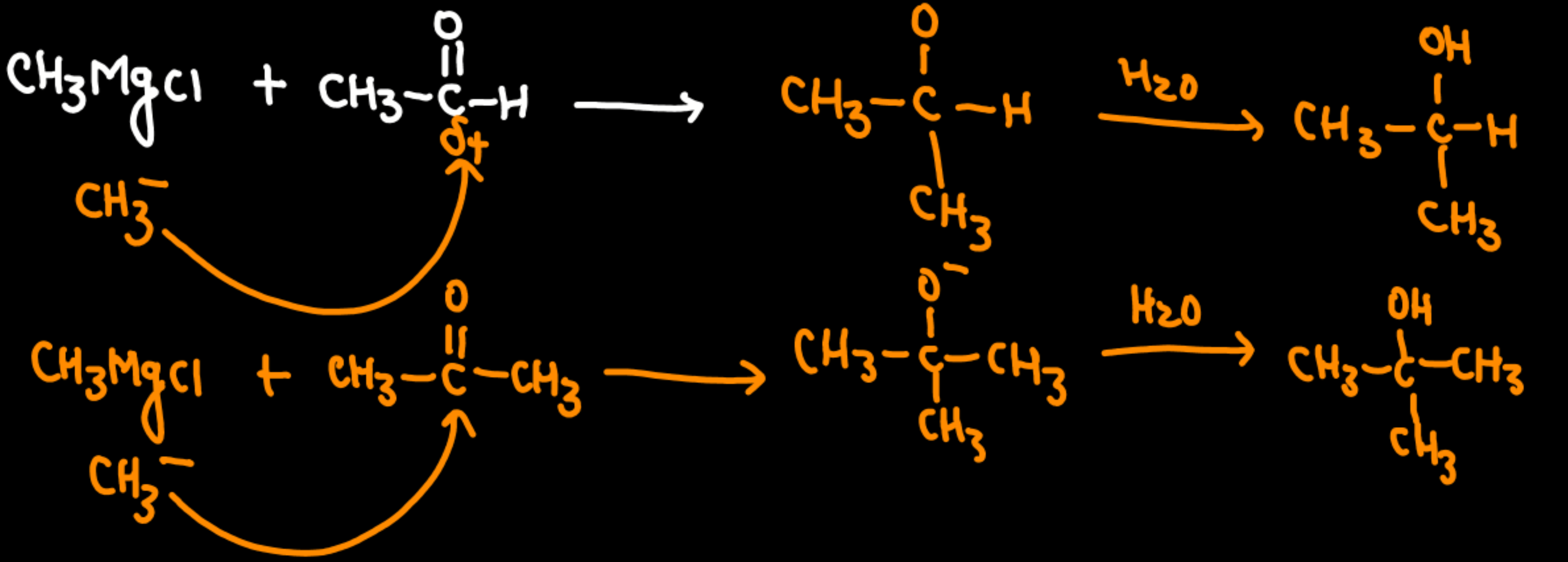


Grignard Reagent

$$R-X \xrightarrow[\text{ether}]{Mg} R-MgX \longrightarrow \text{releases } R^{-}$$

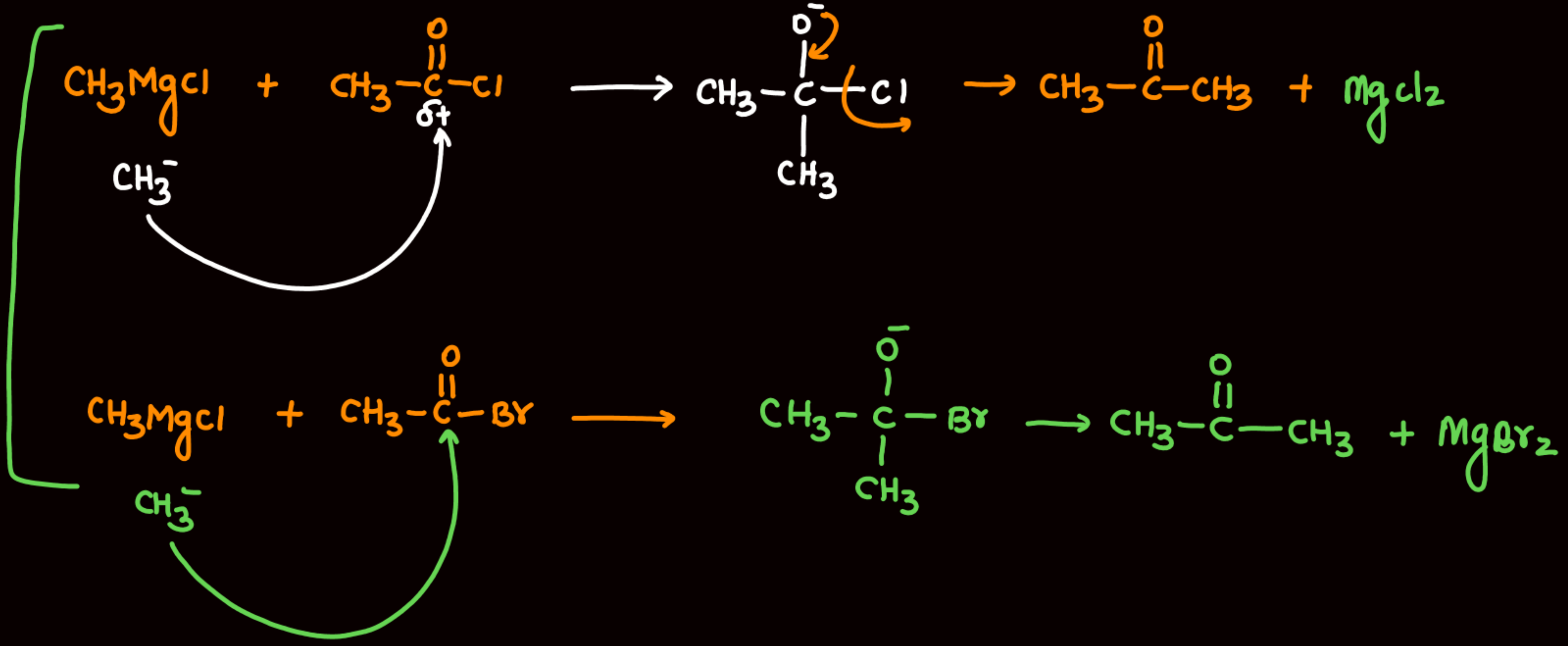
Grignard





nucleophillic addition reaction

nucleophillic
addition
elimination
Reaction



Reactions with Metals: -

Grignard Reagent:

(i) Examples of nucleophilic addition reaction:

Ques.

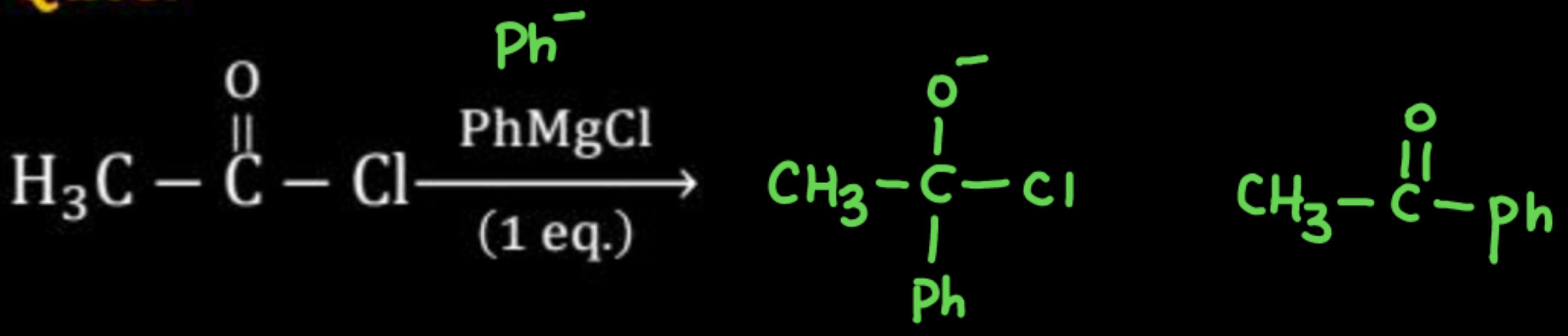
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H + \underset{CH_3^-}{H_3C-MgCl} \xrightarrow{H_2O} H-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H \longrightarrow H-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H$$

Ques.

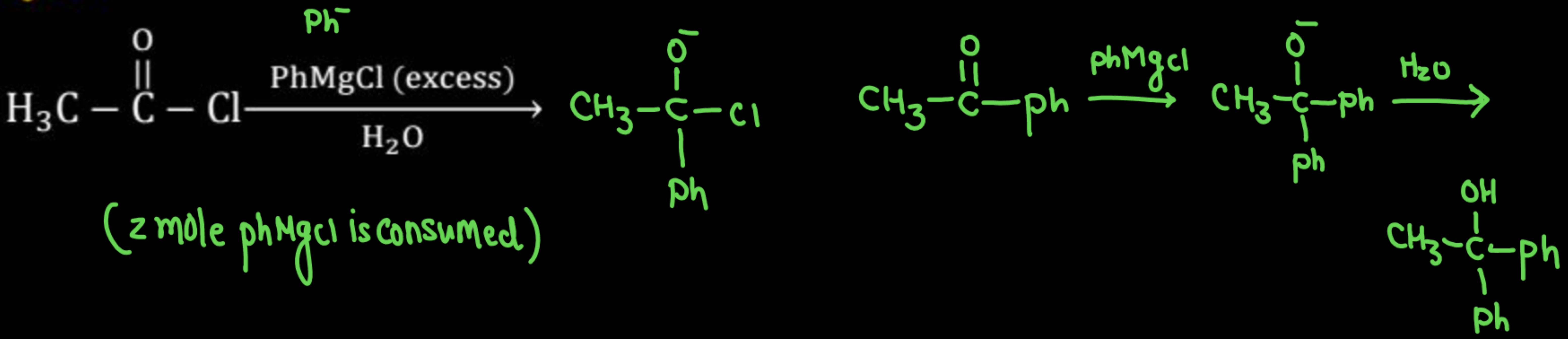
$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H + \underset{CH_3-CH_2^{\ominus}}{H_3C-CH_2-MgBr} \xrightarrow{ROH} CH_3-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle CH_2-CH_3}{|}}{C}}-H \longrightarrow CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-CH_3$$

(ii) Examples of nucleophilic addition elimination reaction:

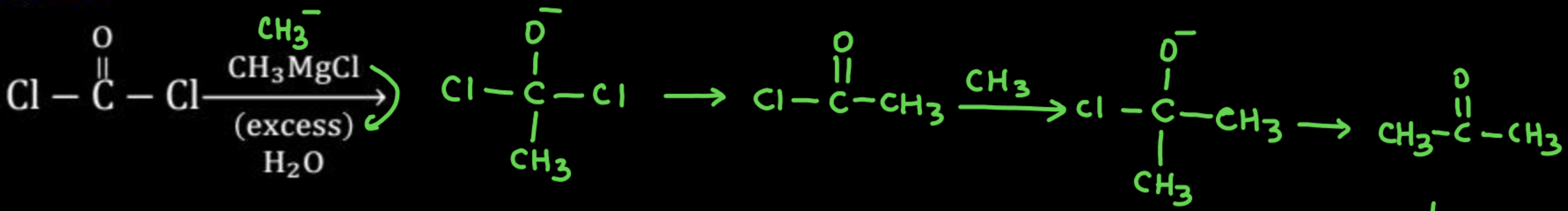
Ques.

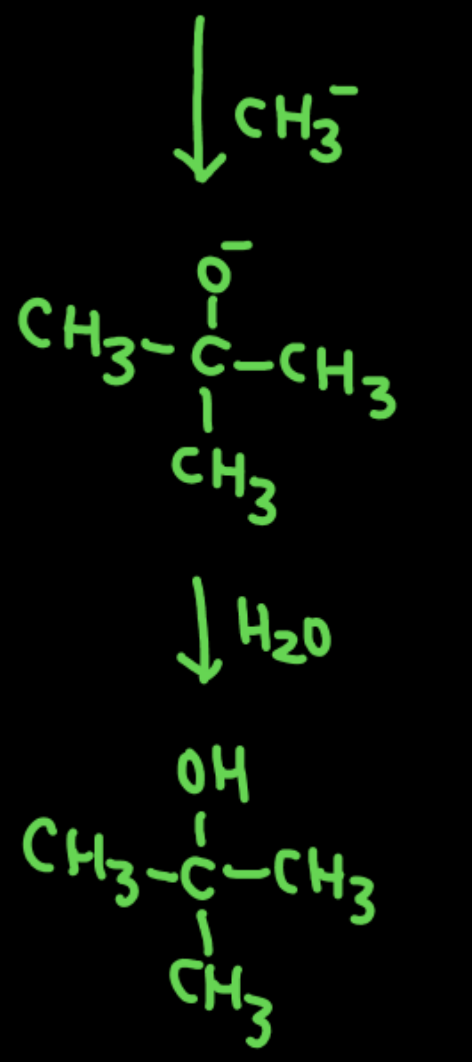


Ques.



Ques.





3 mole CH_3MgCl is consumed.

Examples of Acid-Base Reaction:

Ques.

$$H_3C - MgCl + ROH \longrightarrow CH_4 + Mg\begin{matrix} Cl \\ OR \end{matrix}$$

CH_3^-

Ques.

$$H_3C - CH_2 - MgCl + H - OH \longrightarrow CH_3-CH_3 + Mg\begin{matrix} Cl \\ OH \end{matrix}$$

$CH_3-\overset{\ominus}{C}H_2$

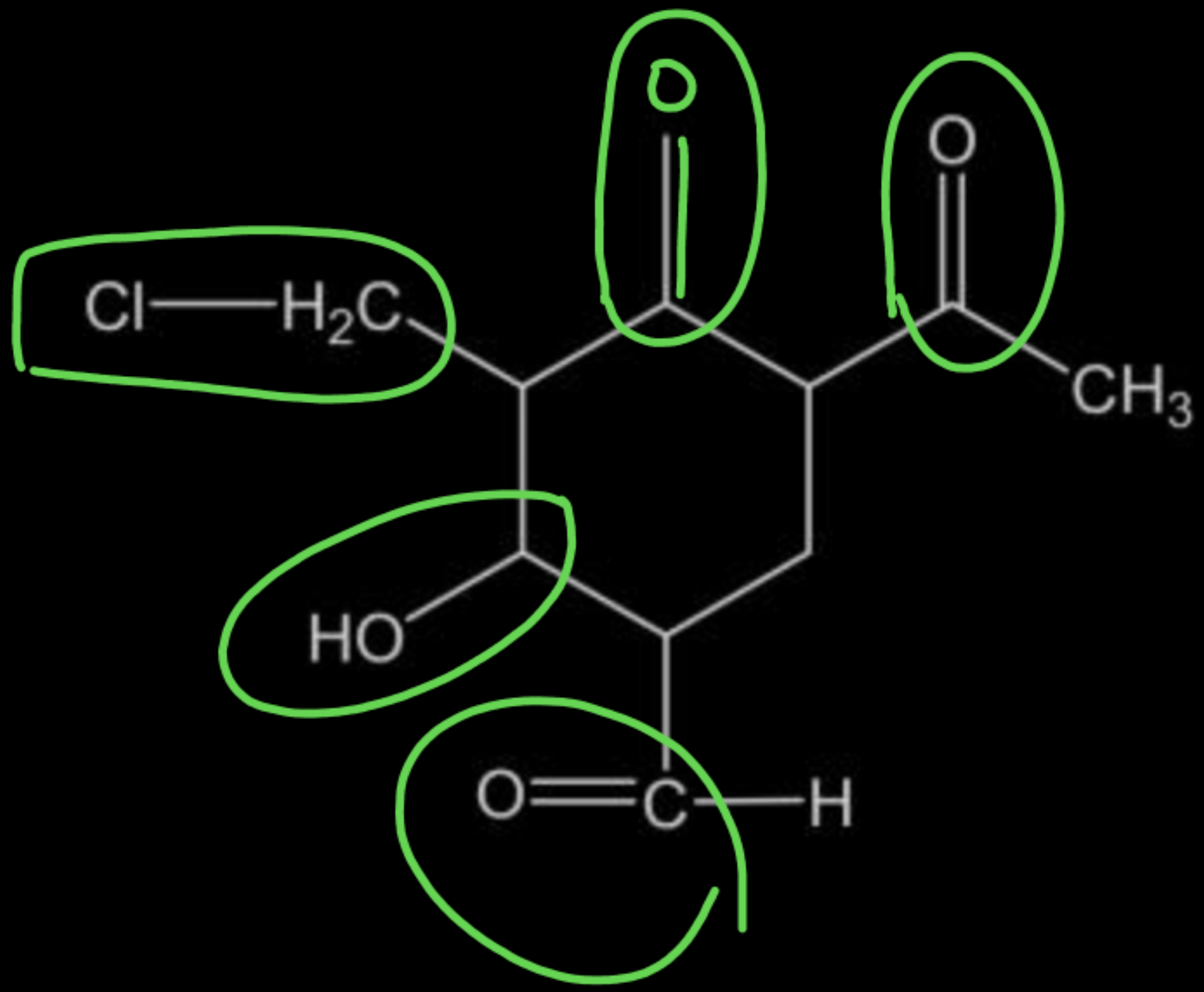
Ques.



$$+ H_3C - Br \xrightarrow[S_N2]{\text{dry ether}}$$

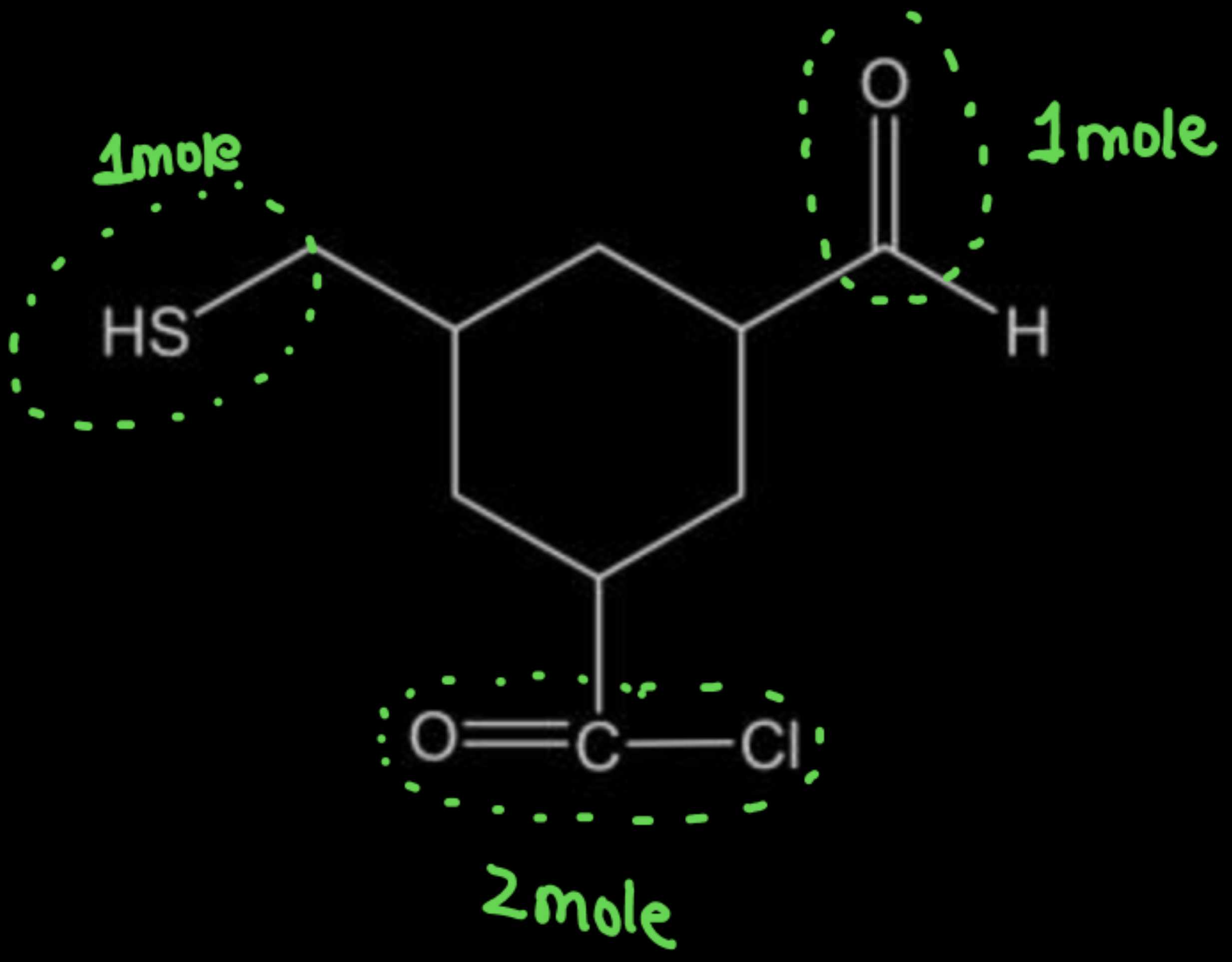
Ques. How many equivalent of Grignard reagent is used in the following compound?

5 mole Grignard



Ques. How many equivalent of Grignard reagent is used in the following compound?

4 mole Grignard





Methods of Preparation of Haloarenes

① Benzene ⟶ Haloarene

② Phenol ⟶ Haloarene

③ Benzene Carboxylicacid → Haloarene

④ Benzene diazonium salt → Haloarene

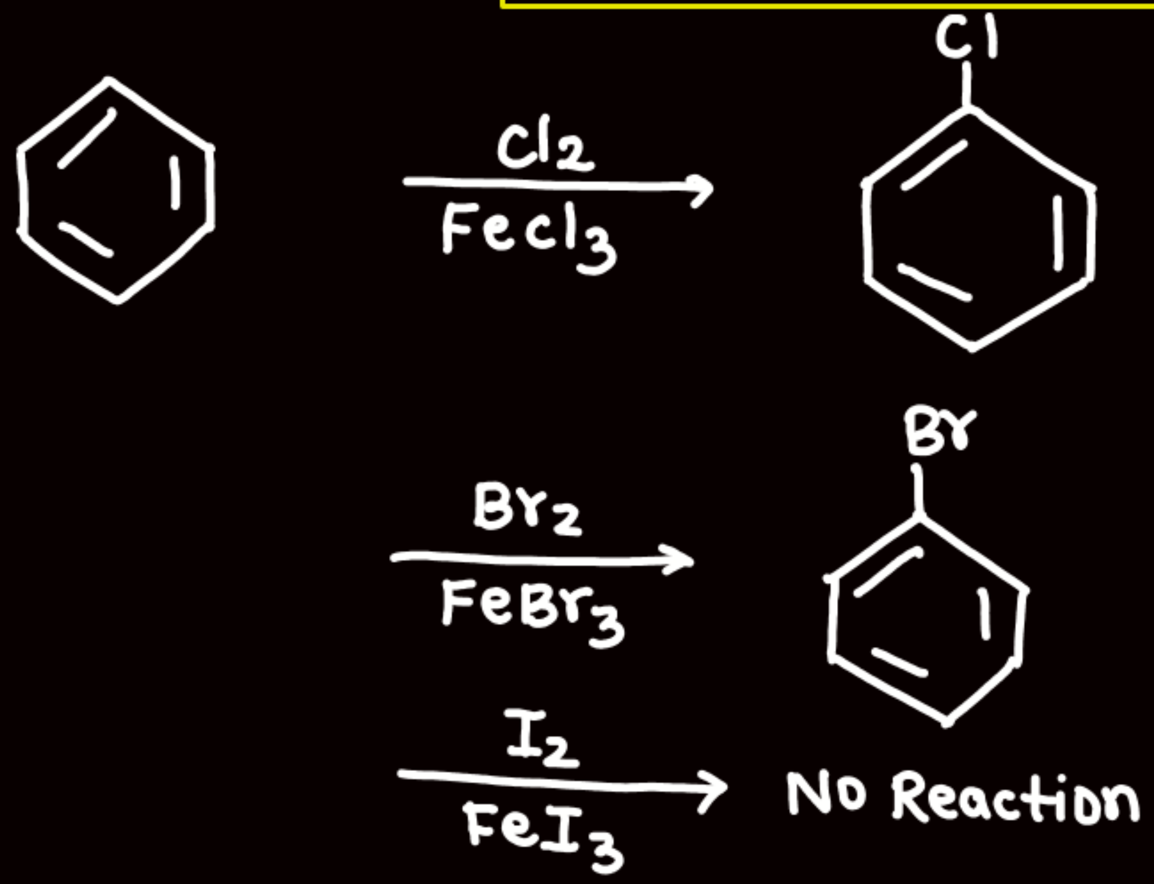
(i) Gatterman Reaction

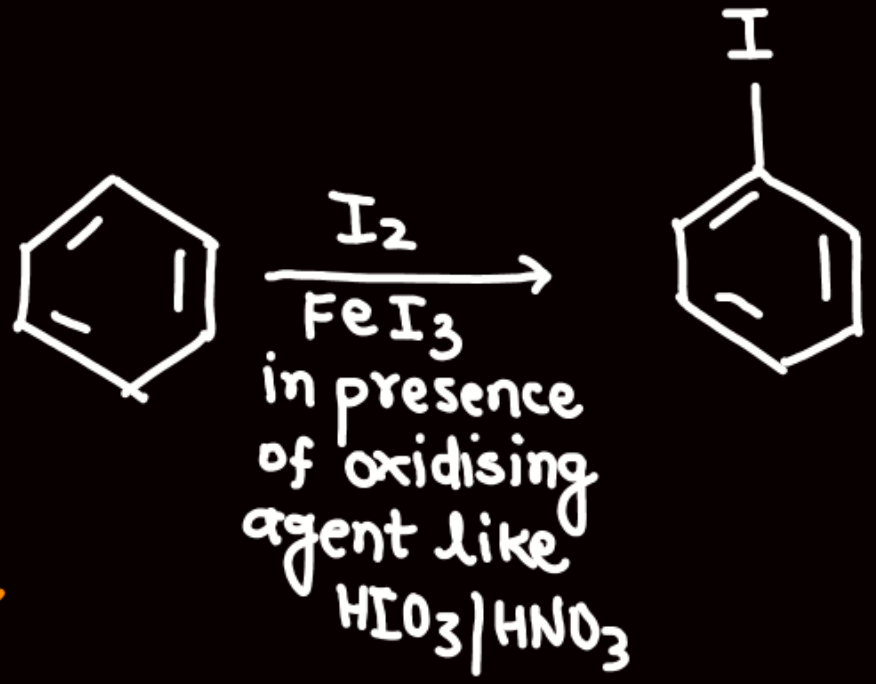
(ii) Sandmayer Reaction

⑤ Reaction with KI → Formation of IodoBenzene

⑥ Balz Schiemann Reaction

Benzene ⟶ Haloarene



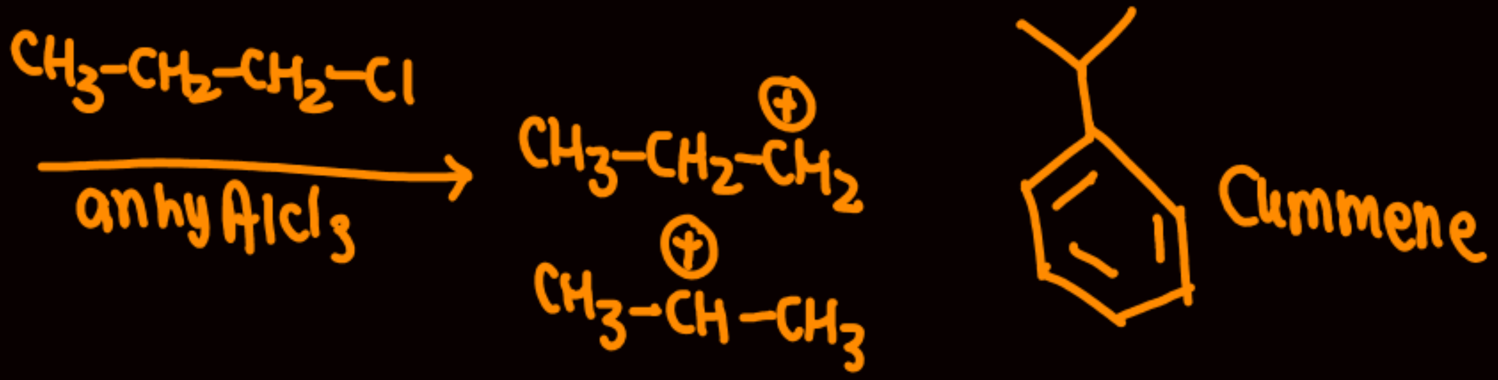


Extra Que

Friedal Craft alkylation

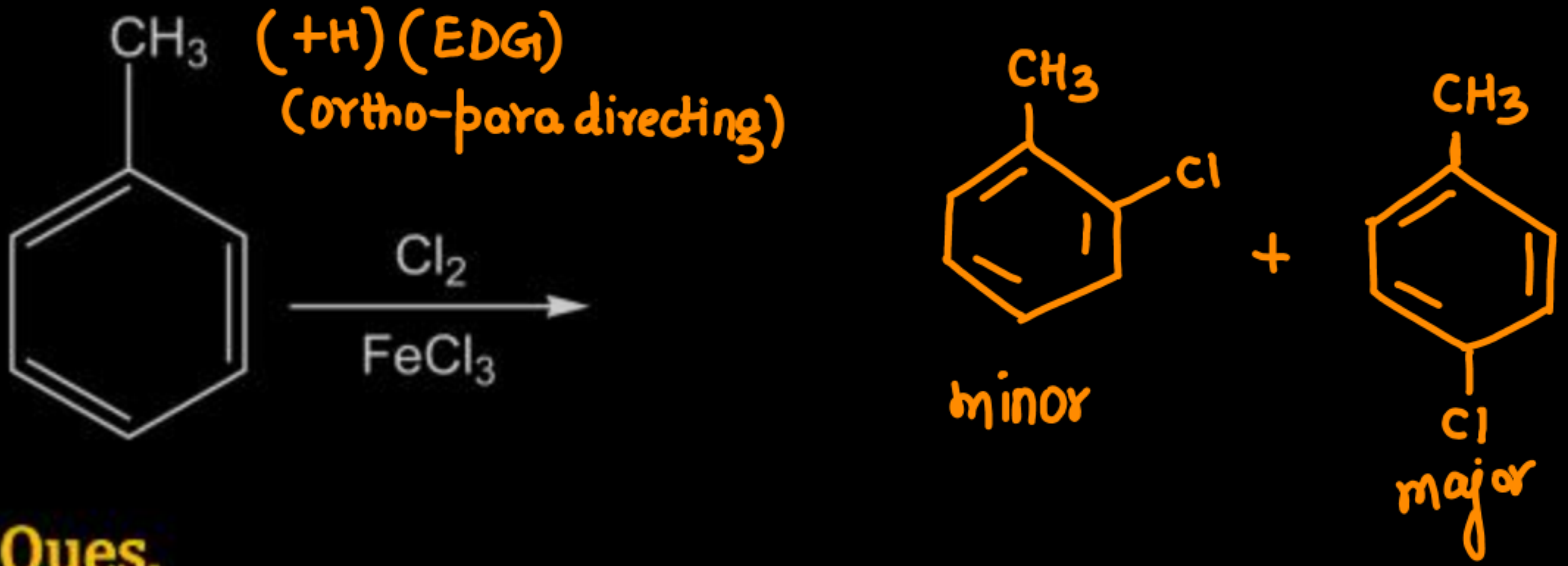


Friedal Craft alkylation

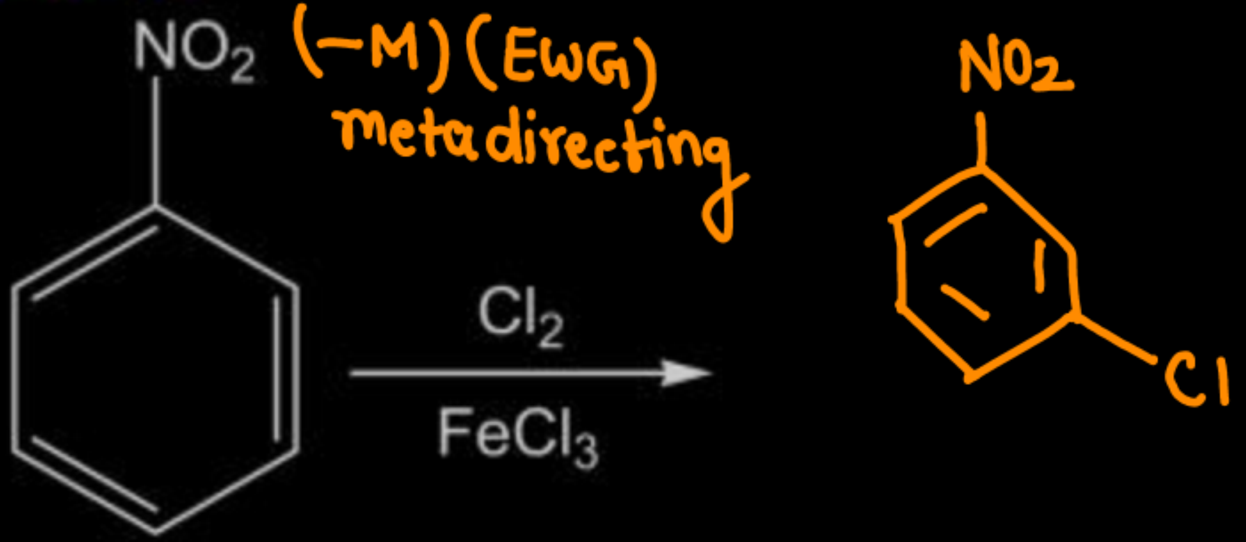


Examples:

Ques.

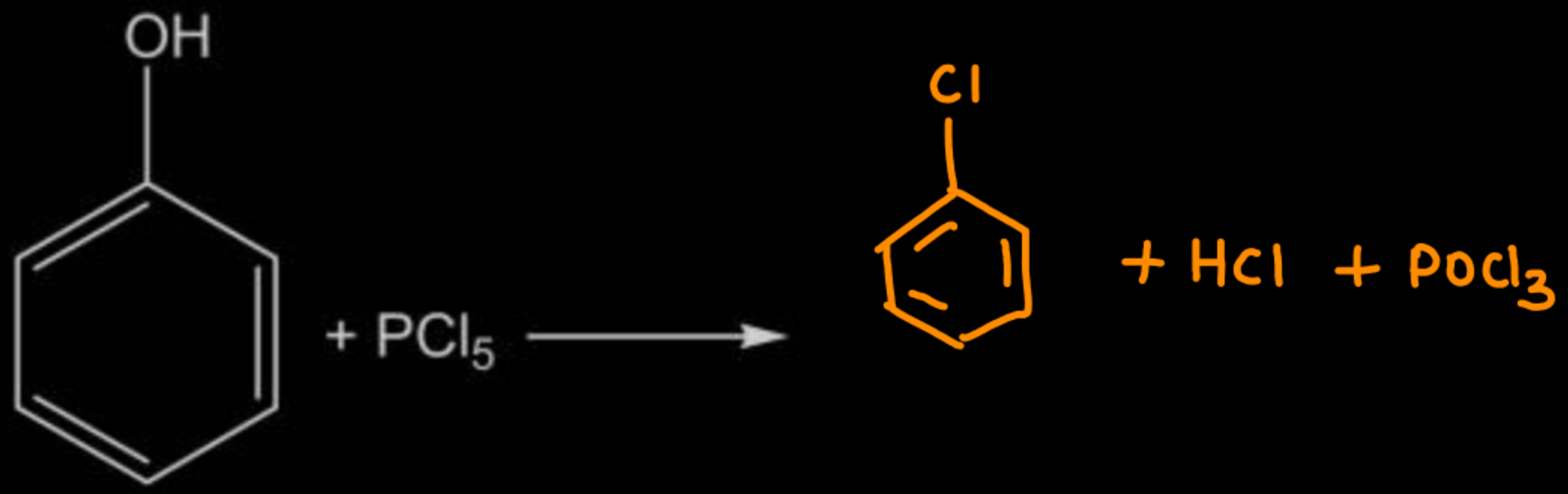


Ques.



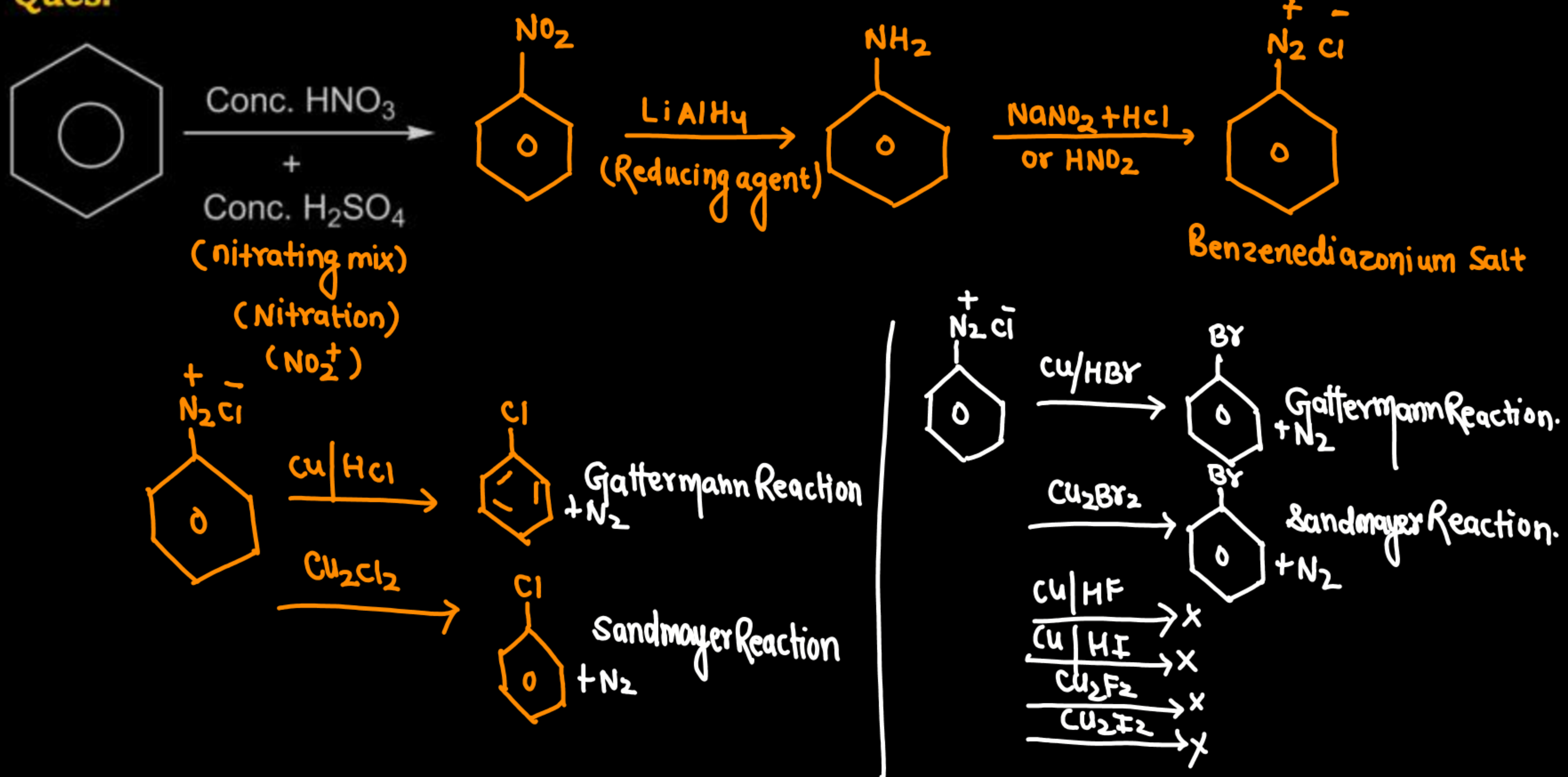
From Phenol:

Ques.

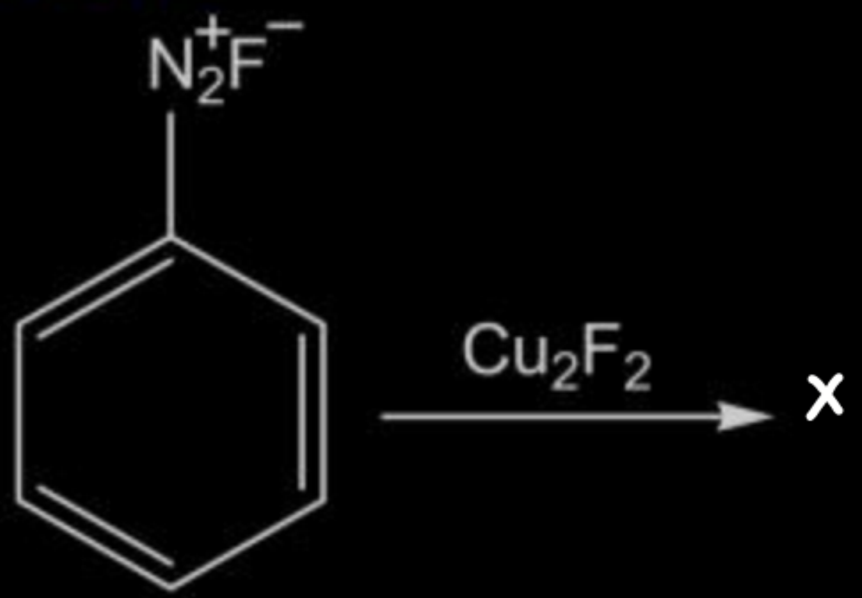


From Benzene Diazonium Salt:

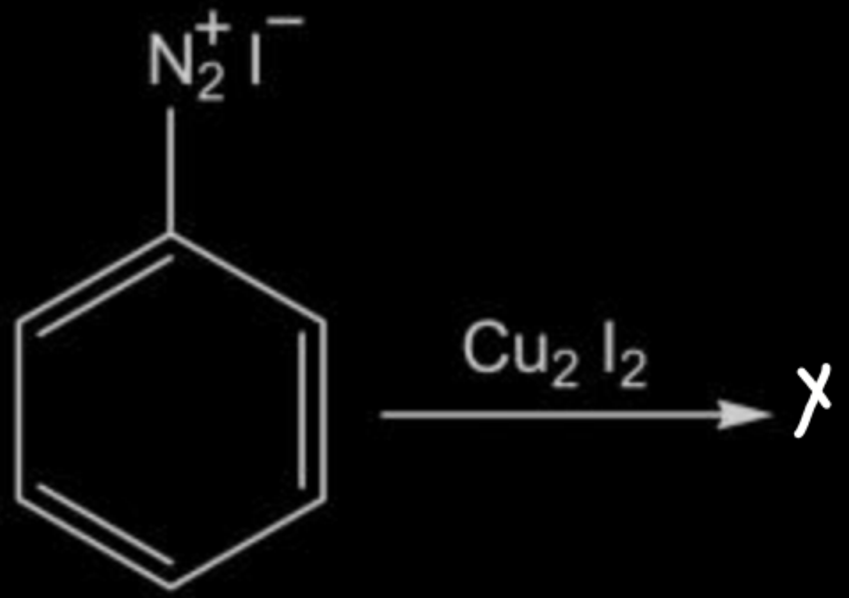
Ques.



Ques.

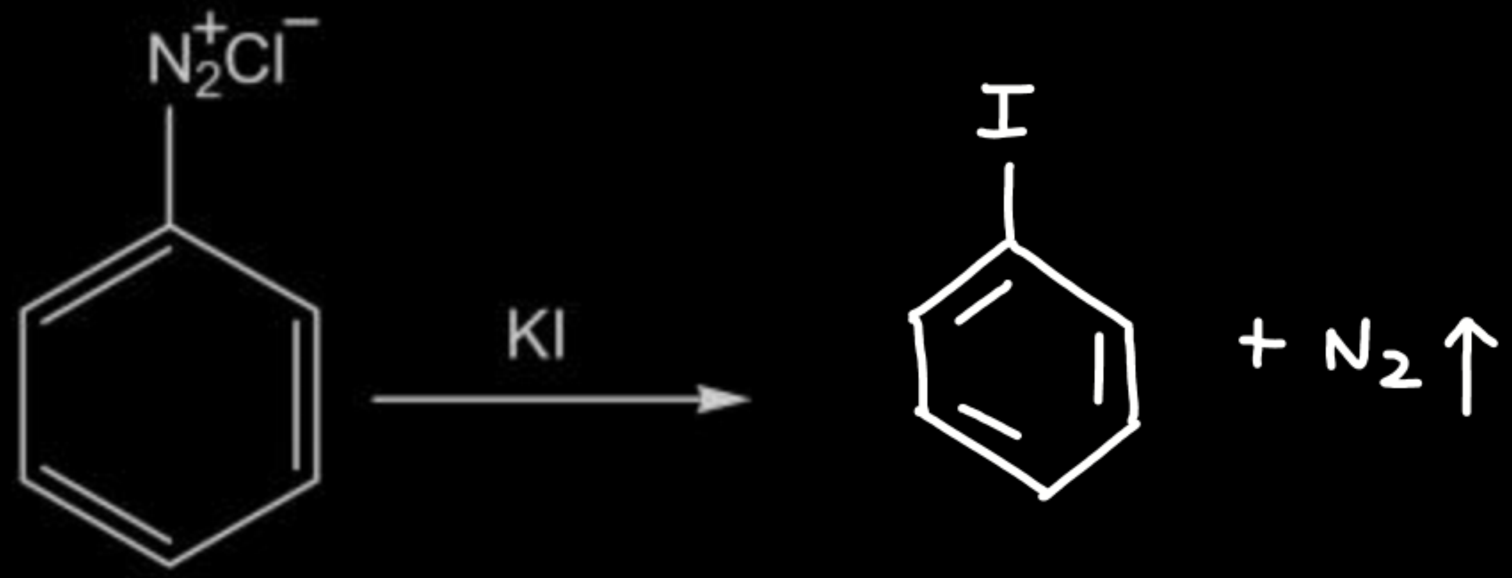


Ques.



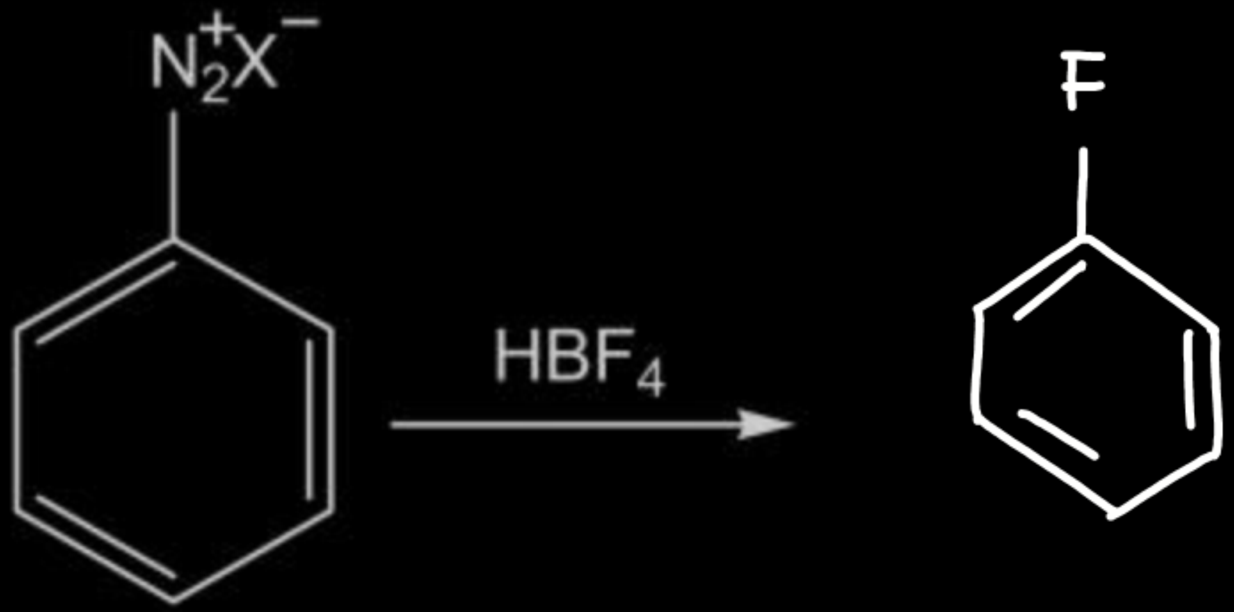
Reaction with KI = (Iodo Benzene):

Ques.



Balz – Schieman Reaction (Fluorobenzene):

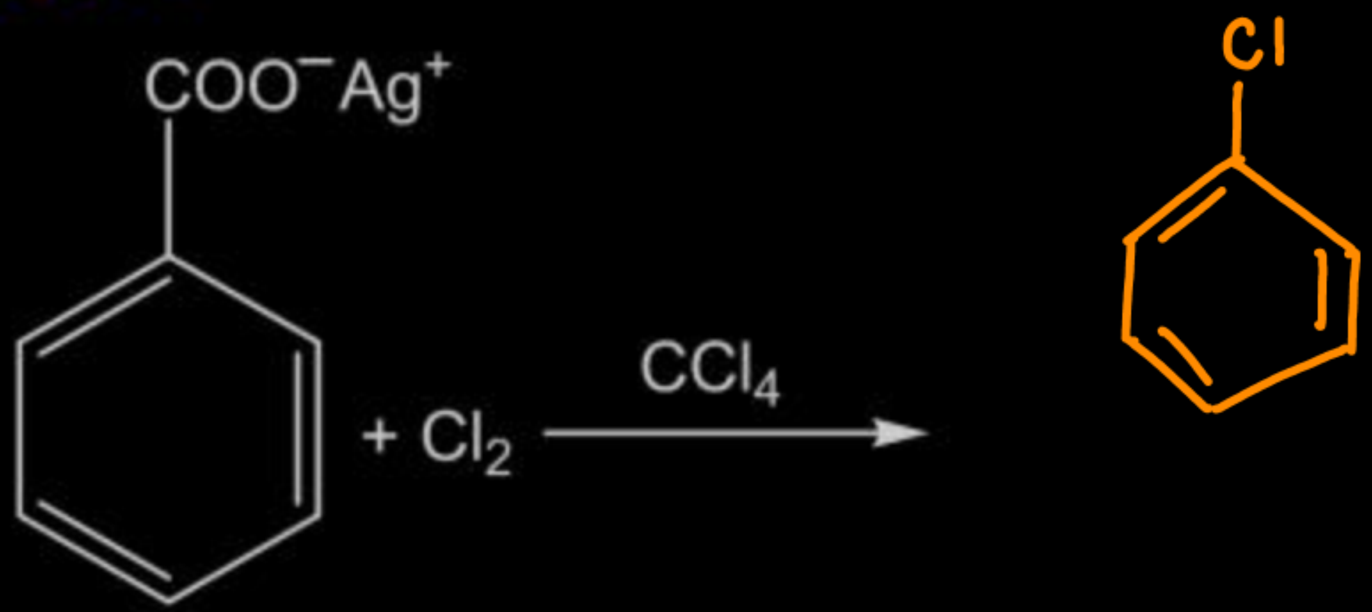
Ques.



From Carboxylic Acid Salt:

Free Radical Mechanism

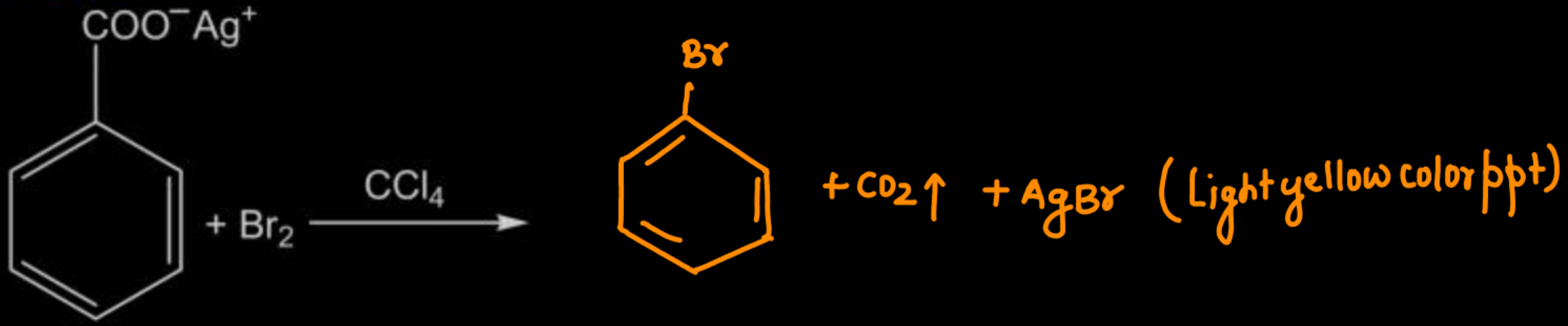
Ques.



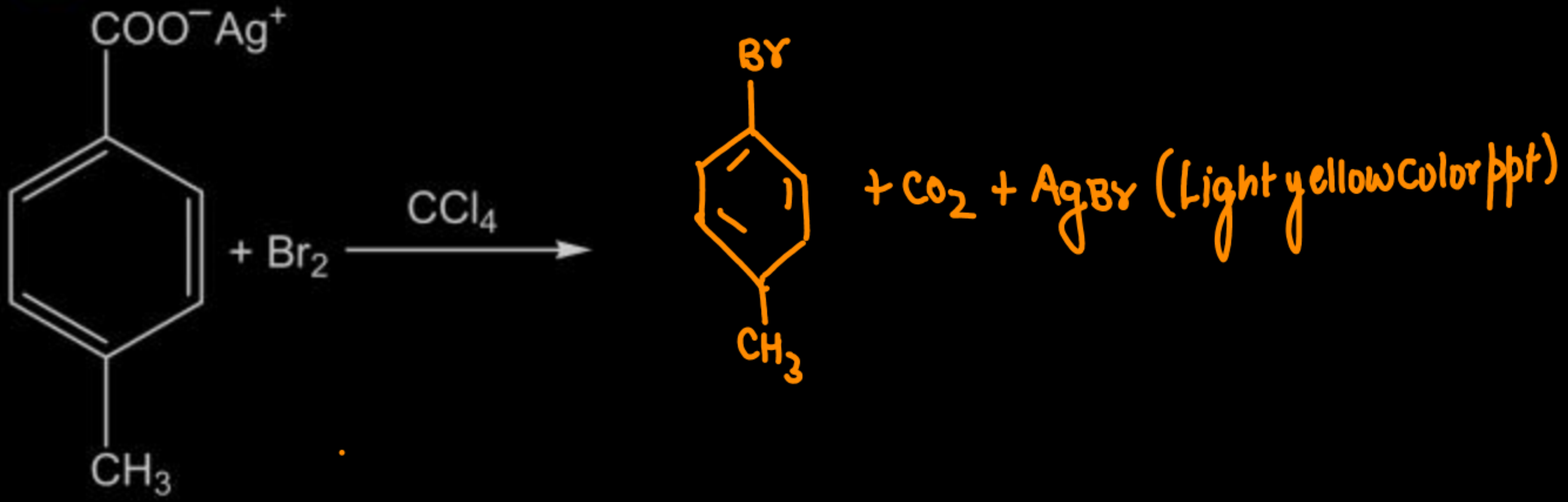
$+ CO_2 + AgCl$ (white color ppt)

AgF	xx
AgCl	White
AgBr	Light yellow
AgI	dark yellow

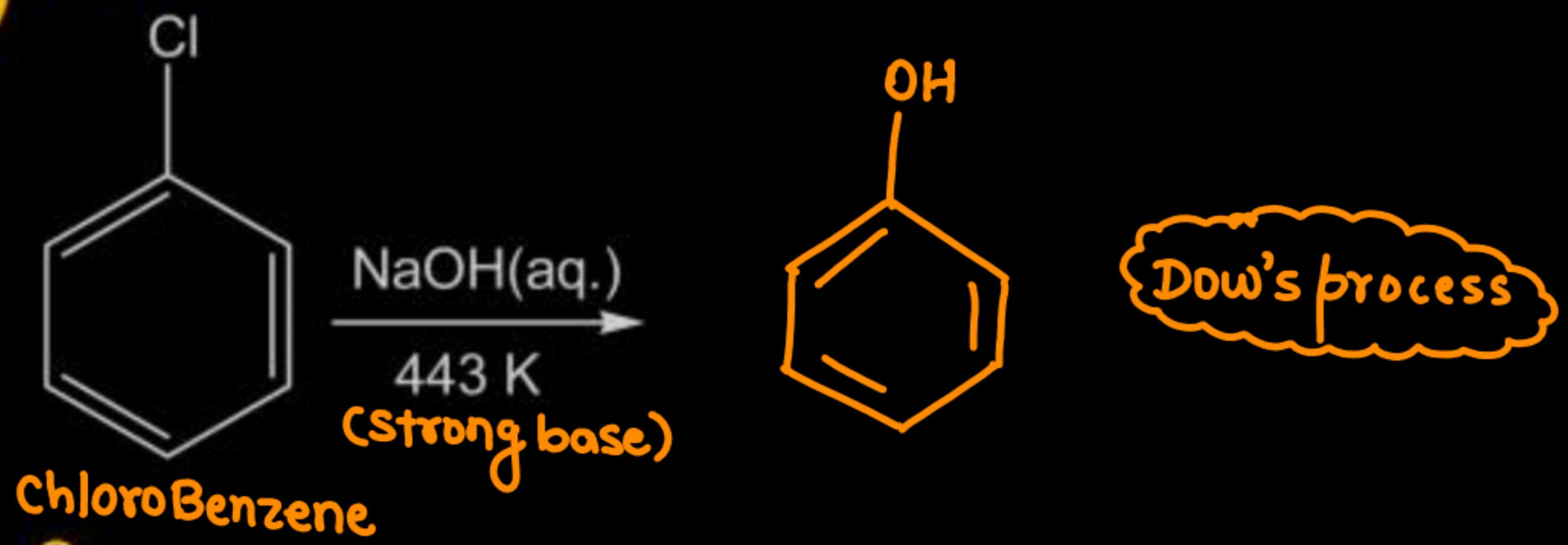
Ques.


COO⁻Ag⁺
+ Br2
CCl4
Br
+ CO2↑ + AgBr (Light yellow color ppt)

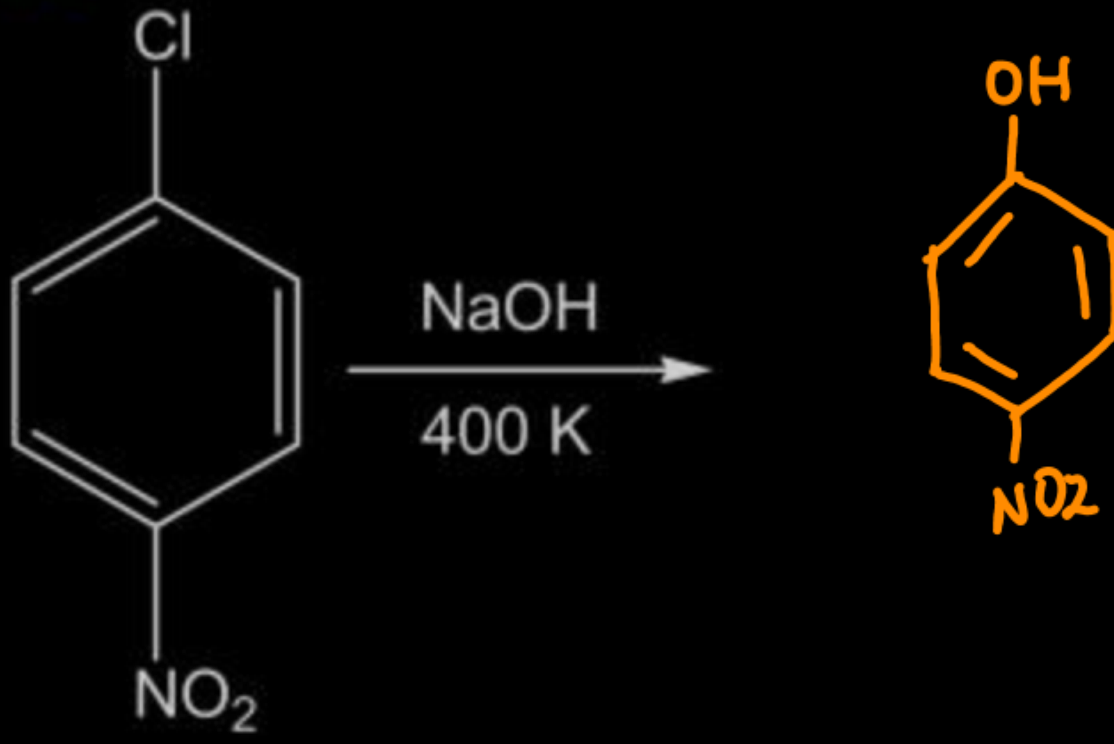
Ques.


COO⁻Ag⁺
+ Br2
CCl4
CH3
Br
CH3
+ CO2 + AgBr (Light yellow Color ppt)

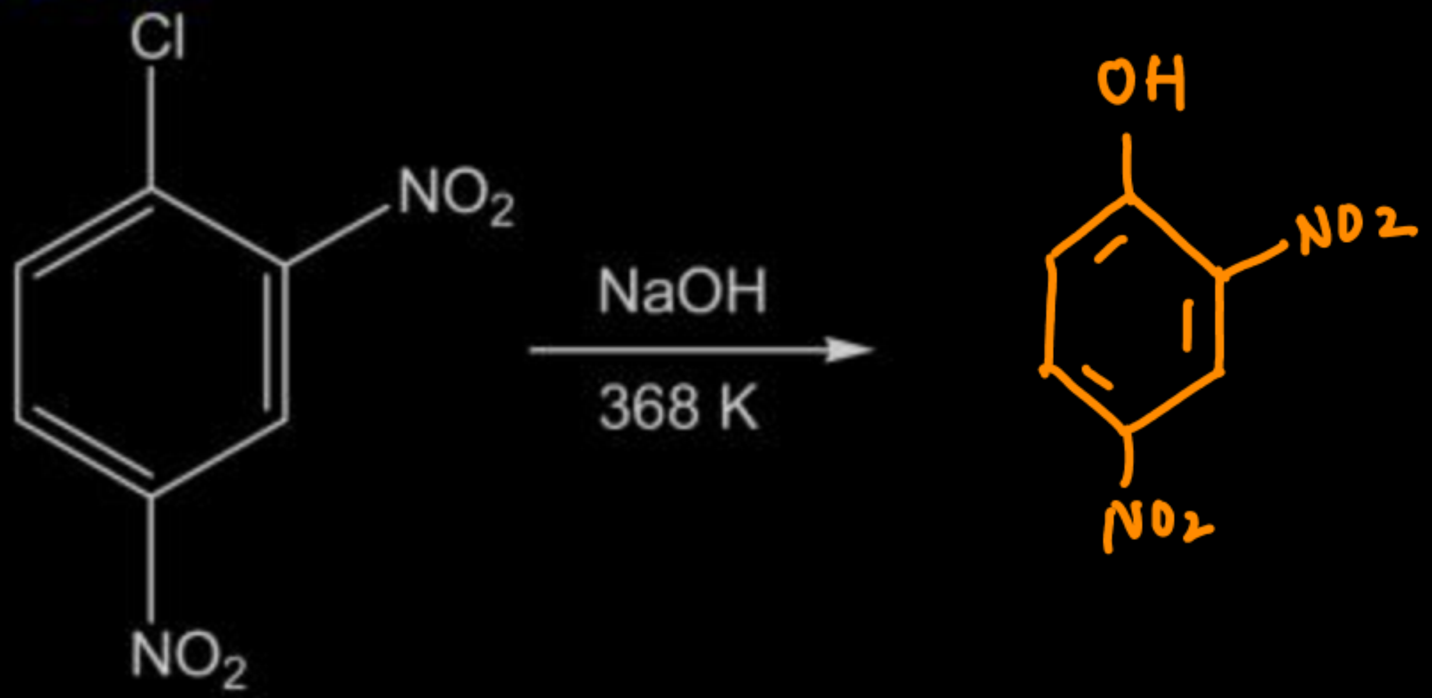
Ques.

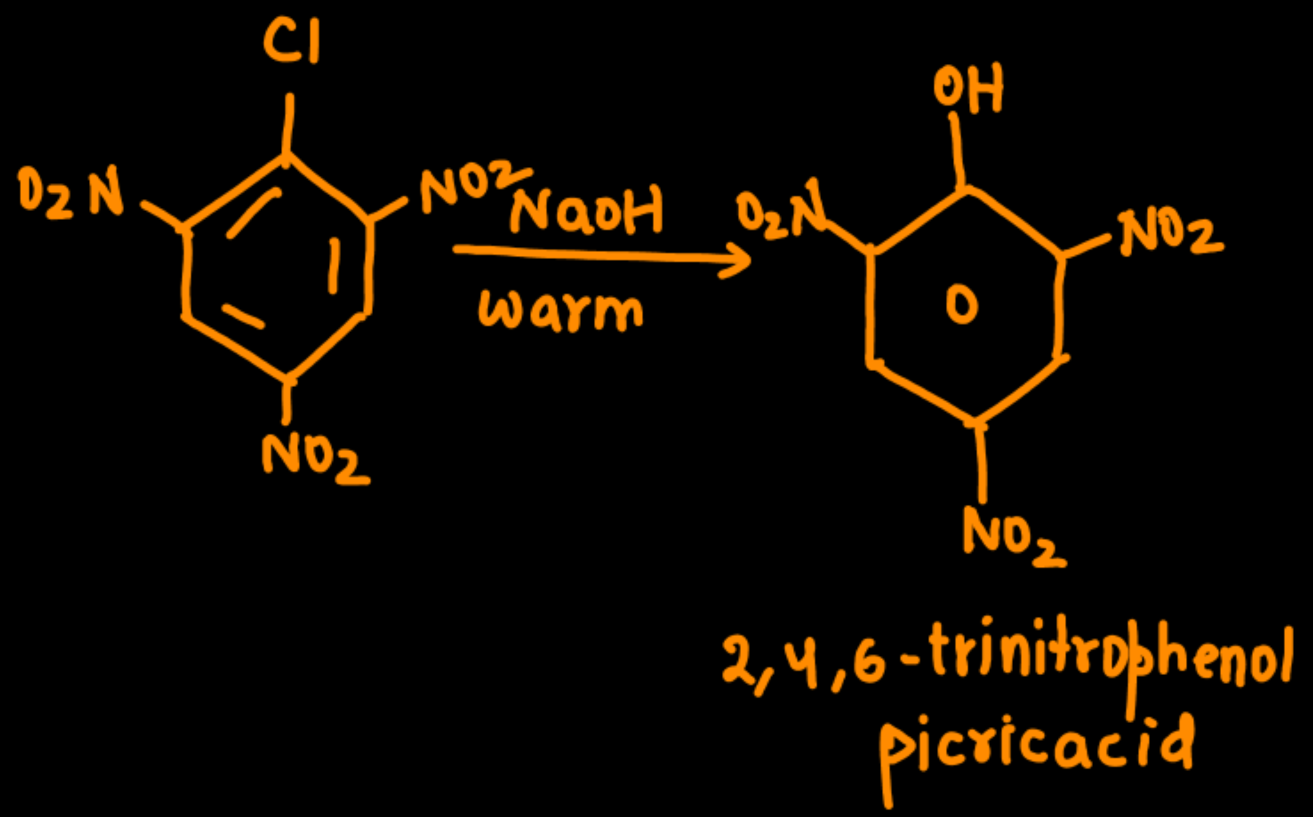

Cl
NaOH(aq.)
443 K
(strong base)
OH
Dow's process
ChloroBenzene

Ques.

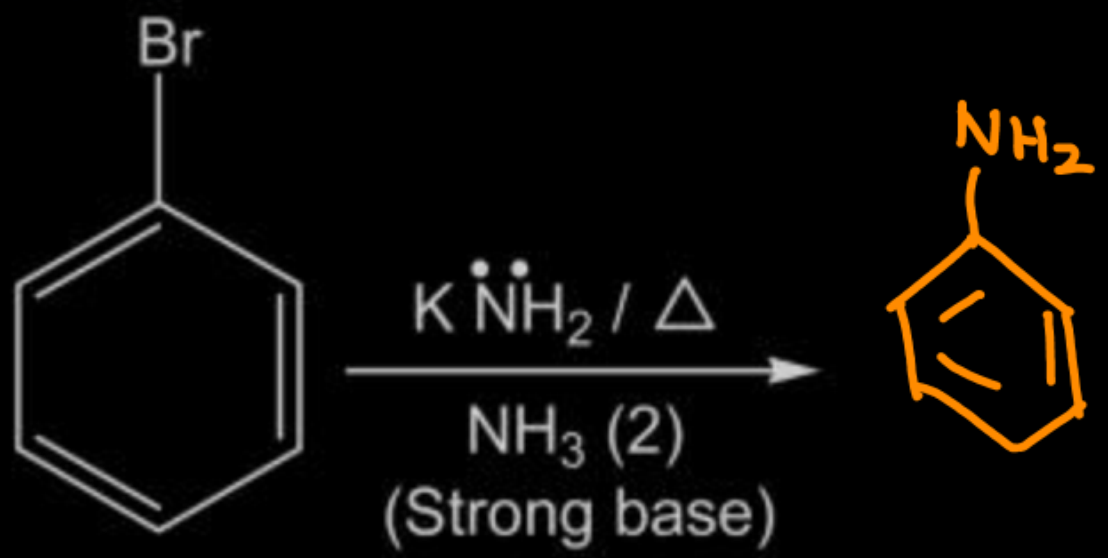

Cl
NaOH
400 K
NO_2
OH
NO2

Ques.

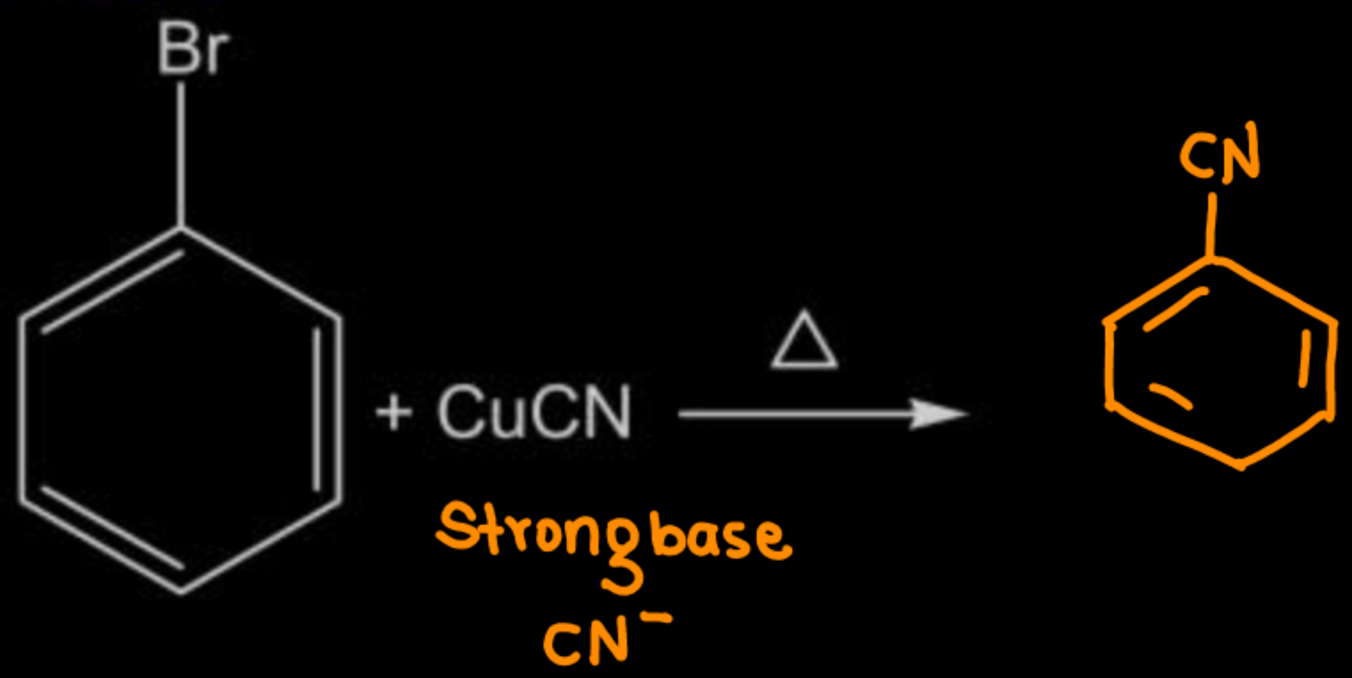

Cl
NO2
NO2
NaOH
368 K
OH
NO2
NO2


Cl
O2N
NO2
NO2
NaOH
warm
OH
O2N
NO2
NO2
2,4,6-trinitrophenol
picricacid

Ques.

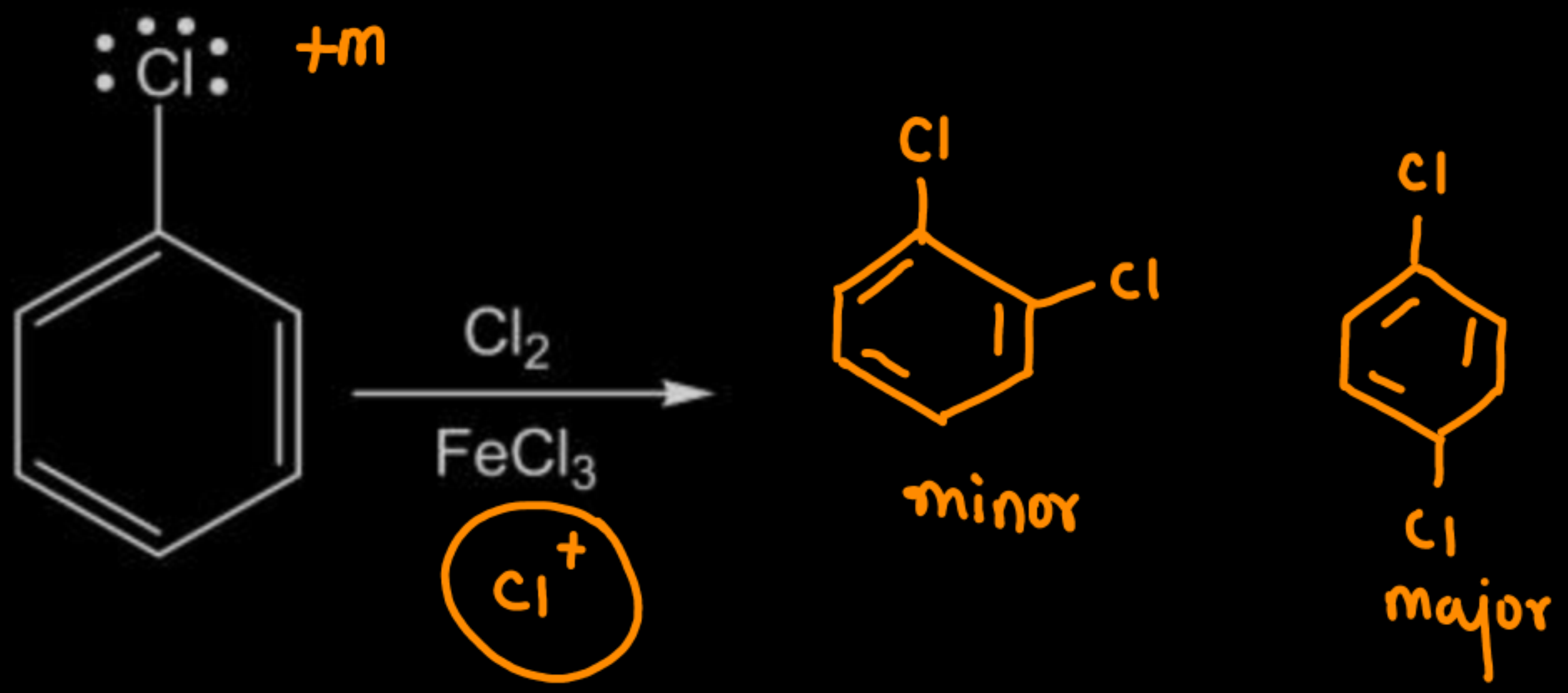

Br
K N̈H2 / Δ
NH3 (2)
(Strong base)
NH2

Ques.



(1) Halogenation:

Ques.



(2) Nitration:

Ques.



(3) Sulphonation:

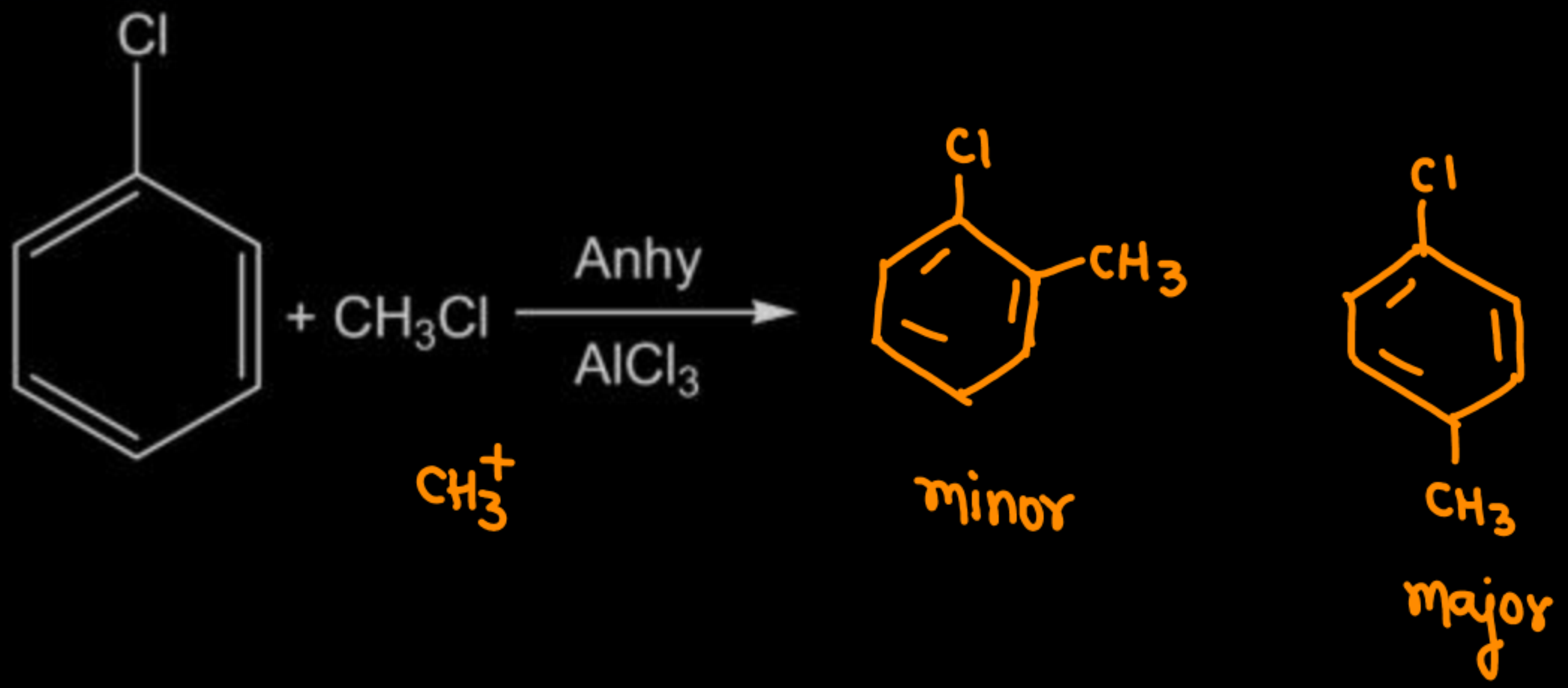
Ques.



(4) Fridal Craft Reaction:

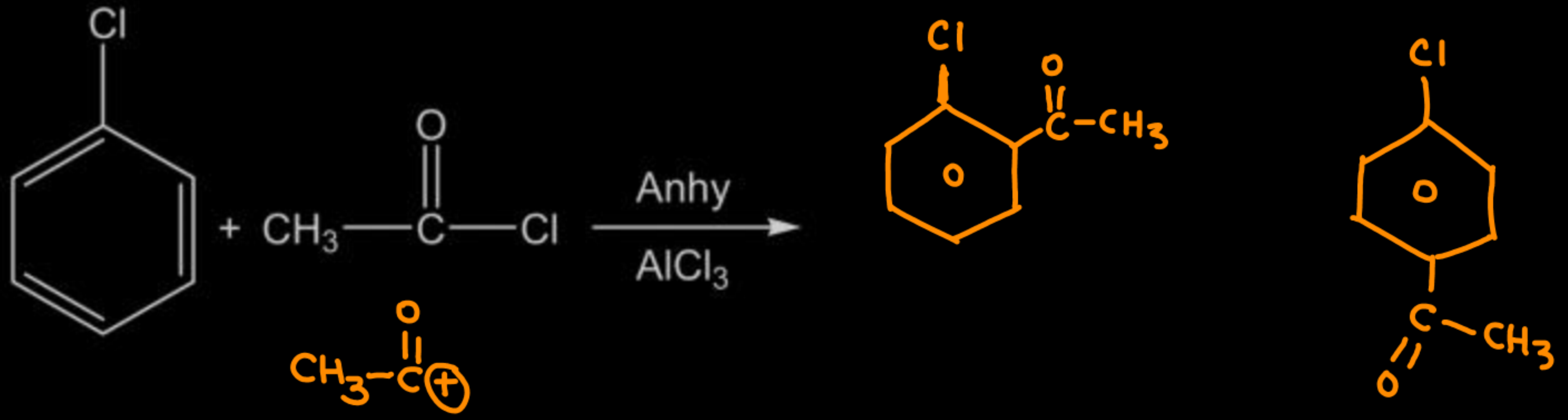
(i) Alkylation ⟶

Ques.



(ii) Acylation

Ques.



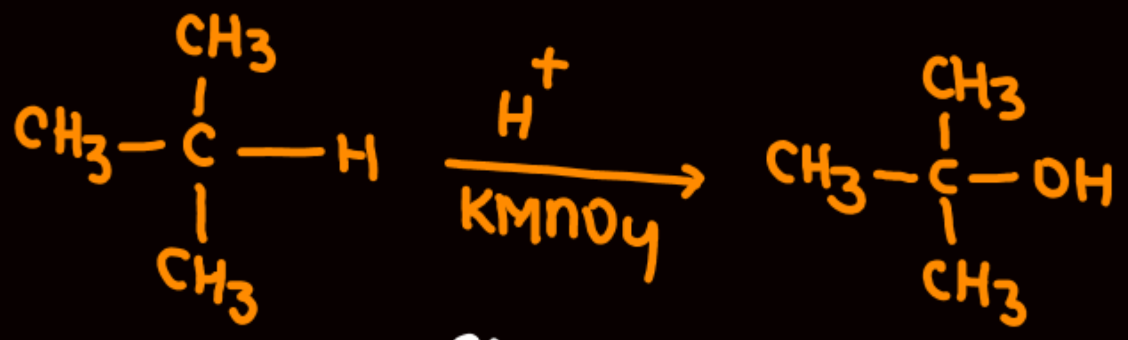
Alcohol Phenol Ether

Method of preparation

1. Alkane → Alcohol
2. Alkene → Alcohol
   PPCH
   (i) acid catalysed hydration (Carbocation formation – Rarrangement – OH attack)
   (ii) OMDM (MK Rule)
   (iii) HBO (AMK Rule)
3. alkylhalide → alcohol (PPCH) (SN^1 & SN^2)
4. aldehyde/ketone → alcohol
5. Carboxylic acid & its derivative → alcohol
6. Grignard → alcohol
7. Ester → alcohol
8. primary amine → alcohol

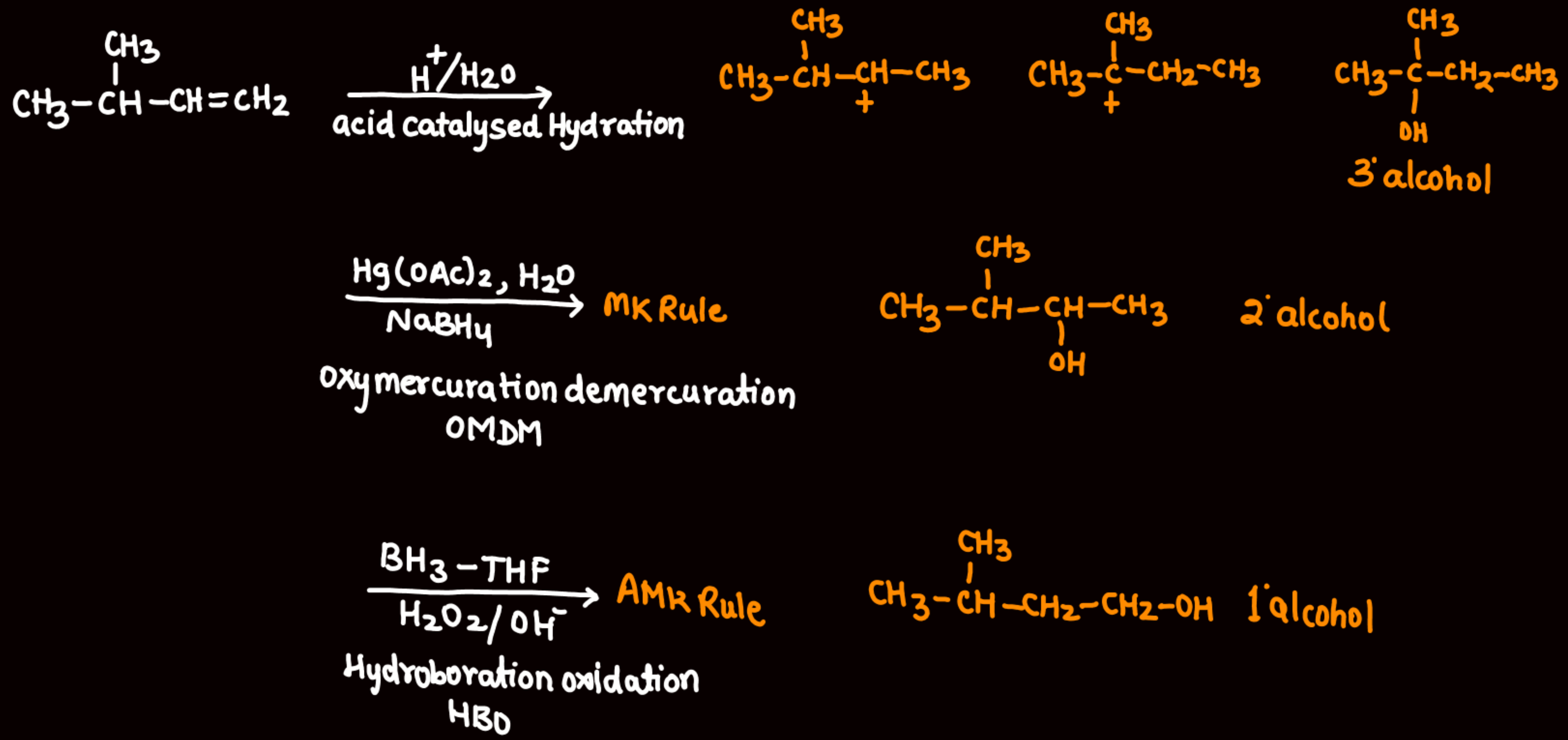
Alkane → Alcohol

Alkane Having $3^\circ H$ (Tertiary alkane) $\xrightarrow[KMnO_4]{H^+}$ alcohol

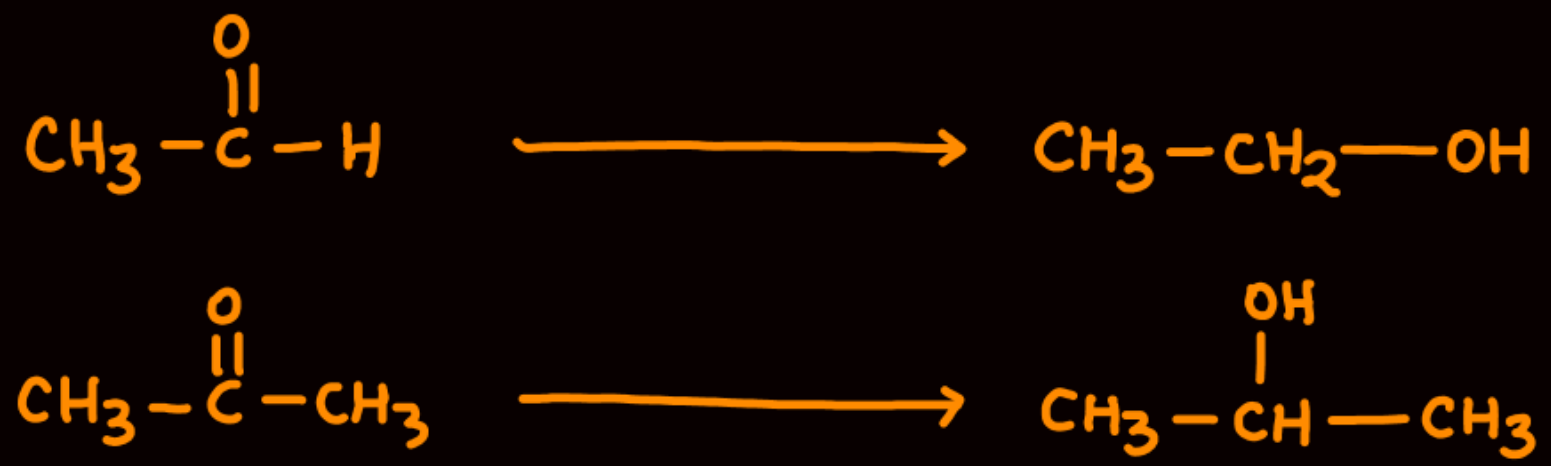


Strong oxidising agent

* Catalytic oxidation


H+/H2O
acid catalysed Hydration
3° alcohol
Hg(OAc)2, H2O
NaBH4
MK Rule
Oxymercuration demercuration
OMDM
2° alcohol
BH3-THF
H2O2/OH-
AMK Rule
Hydroboration oxidation
HBO
1° alcohol

Aldehyde/ketone ⟶ Alcohol



aldehyde — alcohol

Ketone — alcohol

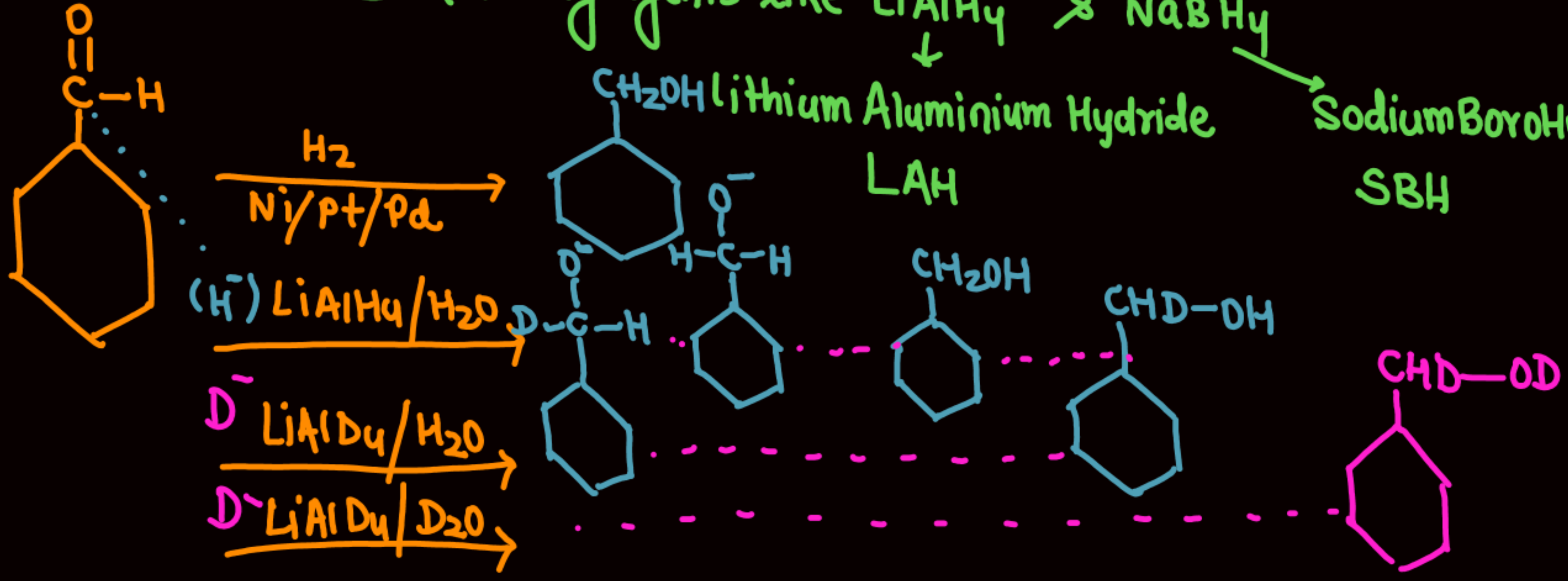
Reducing agent

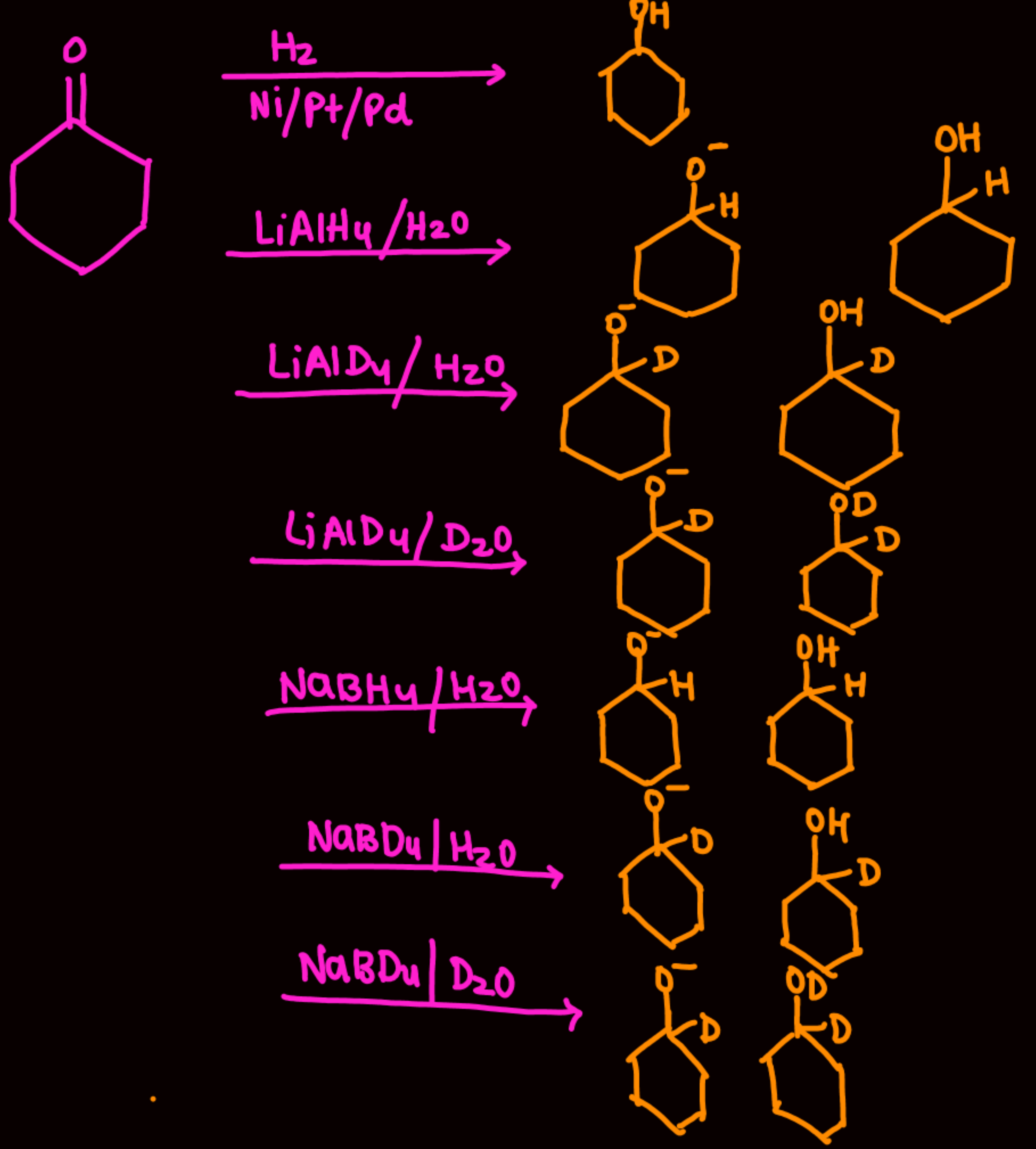
① Catalytic Hydrogenation $\xrightarrow[Ni/Pt/Pd]{H_2}$

② Reducing agents like $LiAlH_4$ & $NaBH_4$

$LiAlH_4$ ↓ Lithium Aluminium Hydride — LAH

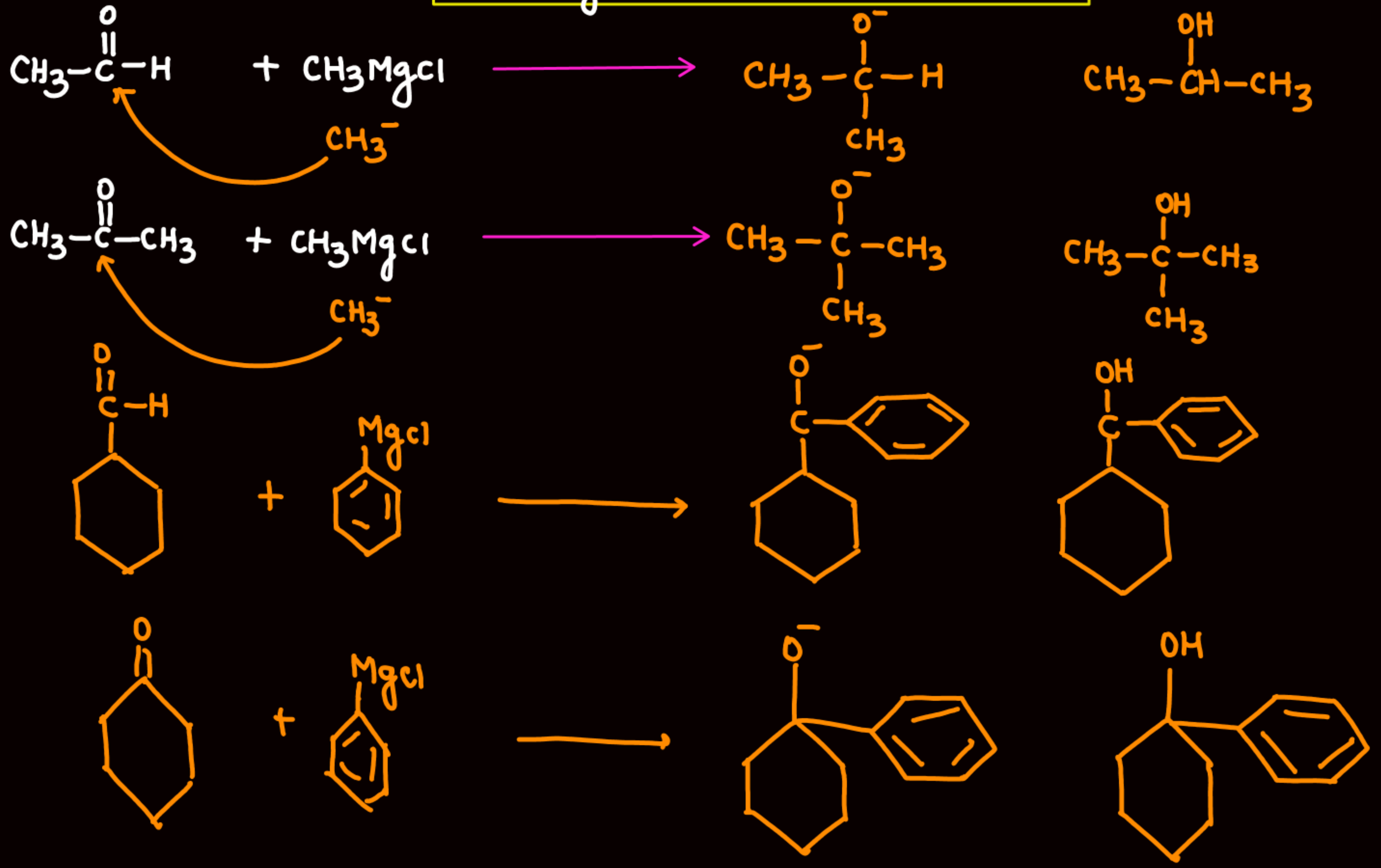
$NaBH_4$ → Sodium BoroHydride — SBH

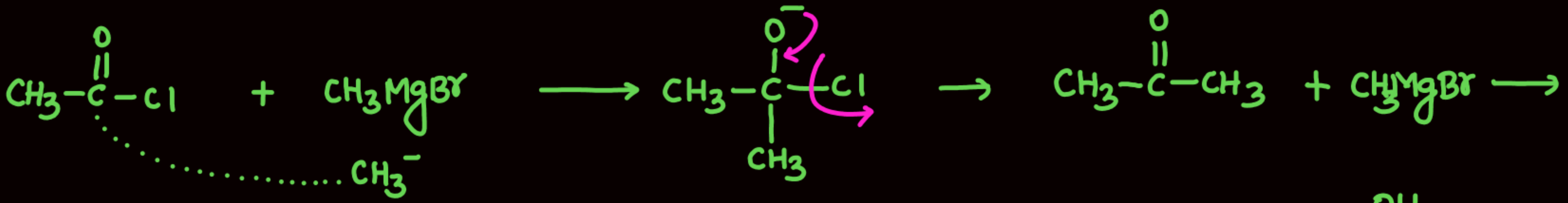


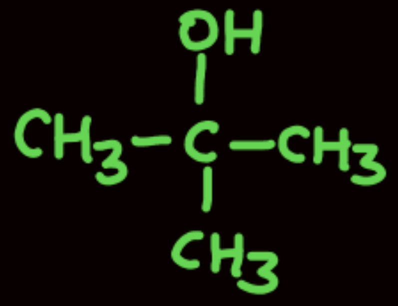


O
H2
Ni/Pt/Pd
OH
LiAlH4/H2O
O−
H
OH
H
LiAlD4/H2O
O−
D
OH
D
LiAlD4/D2O
O−
D
OD
D
NaBH4/H2O
O−
H
OH
H
NaBD4/H2O
O−
D
OH
D
NaBD4/D2O
O−
D
OD
D

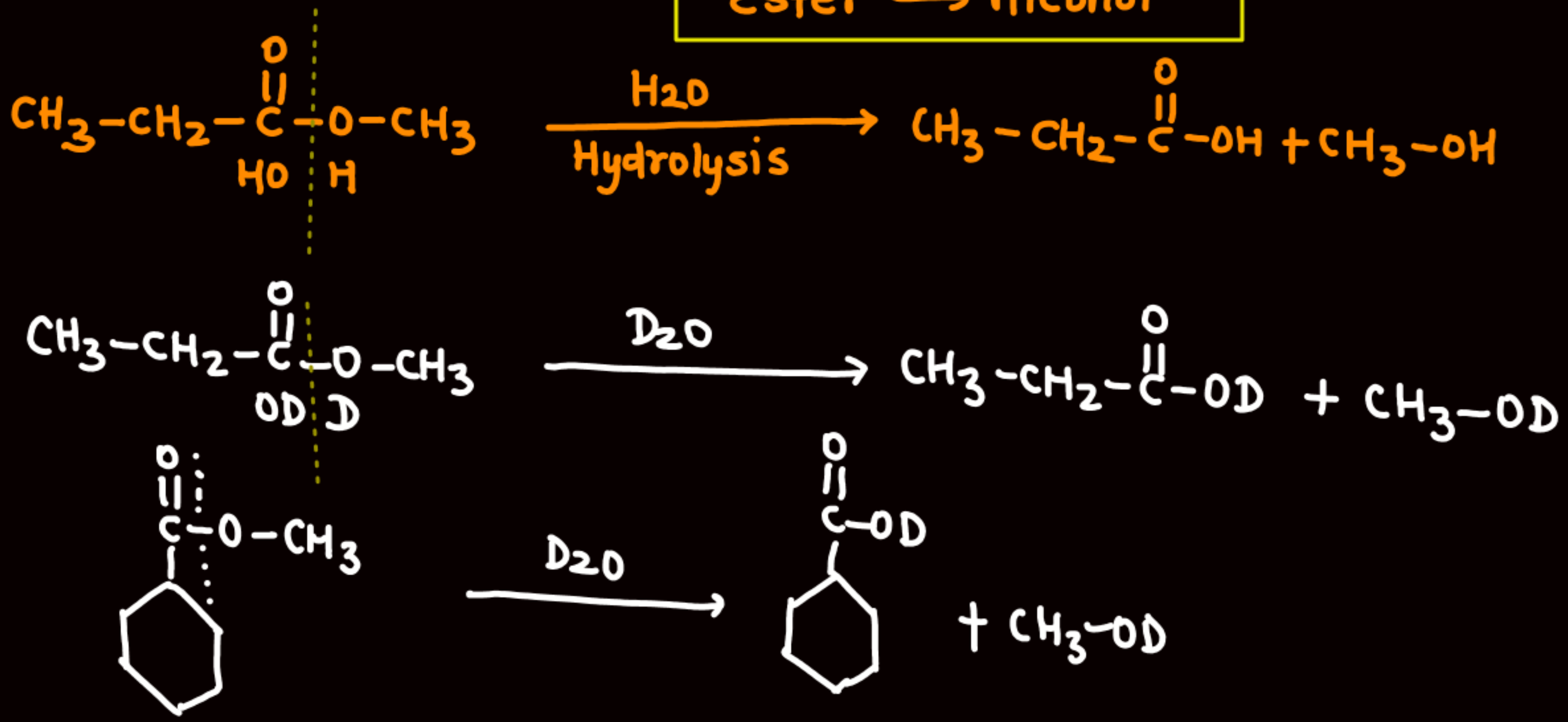
Grignard → alcohol



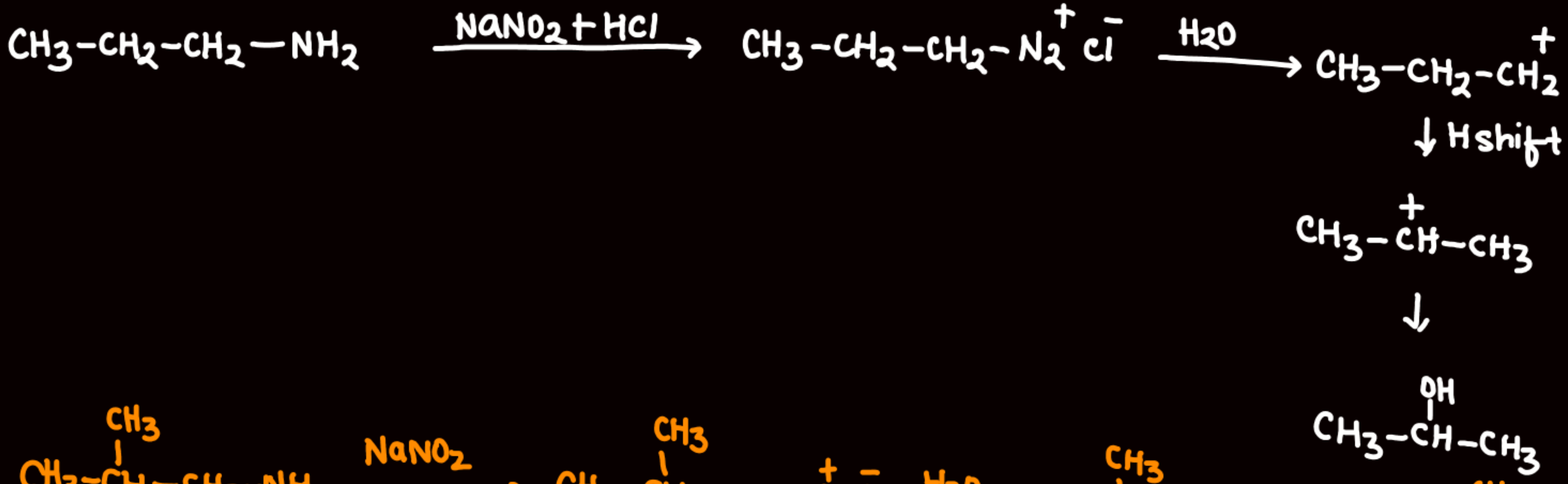


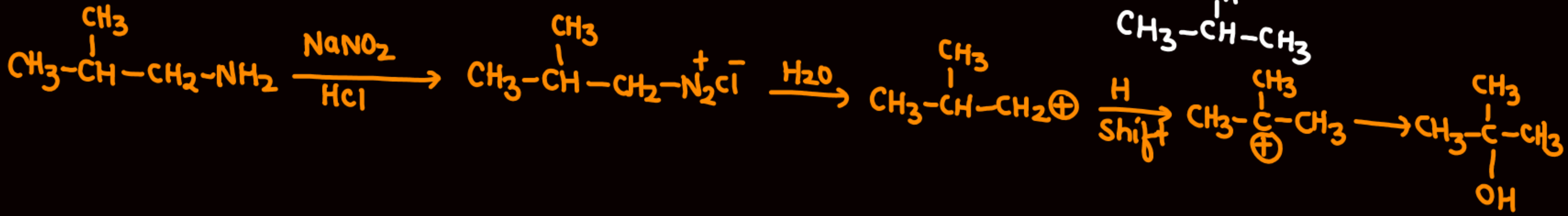


Ester → Alcohol



Primary amine → alcohol (using diazonium salt)





$R-\overset{O}{\overset{\|}{C}}-OH$ ✗ $R-\overset{O}{\overset{\|}{C}}-Cl$ ✓ $R-\overset{O}{\overset{\|}{C}}-NH_2$ ✓ $R-\overset{O}{\overset{\|}{C}}-OR$ ✓

(1) Reduction using Catalytic Hydrogenation:

Catalytic Hydrogenation $\xrightarrow[Ni/Pt/Pd]{H_2}$ easily reduces all $R-\overset{O}{\overset{\|}{C}}-Cl$ / $R-\overset{O}{\overset{\|}{C}}-NH_2$ / $R-\overset{O}{\overset{\|}{C}}-OR$

★ except $R-\overset{O}{\overset{\|}{C}}-OH$

H_2 → Reducing agent

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Ni/Pt/Pd]{H_2} CH_3-\overset{OH}{\overset{|}{CH}}-Cl \rightarrow CH_3-CH_2-OH + HCl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{\text{''}} CH_3-CH_2-OH + NH_3$$

$$\underbrace{CH_3-\overset{O}{\overset{\|}{C}}}_{H}-\underbrace{O-CH_3}_{H} \xrightarrow{\text{''}} CH_3-CH_2-OH + CH_3OH$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{(No Reaction)}]{\text{''}} \cancel{CH_3-CH_2-OH + H_2O}$$ ✗

(2) Reduction using $LiAlH_4$: Lithium Aluminium Hydride [LAH]

- Strong Reducing agent
- H^- Release
- It reduces all carboxylic acid as well as its derivative.

$R-\overset{O}{\overset{\|}{C}}-OH$ ✓

$R-\overset{O}{\overset{\|}{C}}-Cl$ ✓

$R-\overset{O}{\overset{\|}{C}}-NH_2$ ✓

$R-\overset{O}{\overset{\|}{C}}-OR$ ✓

<u>Note</u> $NaBH_4$ (mild Reducing agent) → It reduces only $R-\overset{O}{\overset{\|}{C}}-Cl$.



Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH\,/\,Cl\,/\,\ddot{N}H_2\,/\,OR \xrightarrow{LiAlH_4}$$ ✓

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[\text{(ii) } H_2O\,/\,H^+]{\text{(i) } NaBH_4}$$ ✓

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH/NH_2/OR \xrightarrow[\text{② } H_2O/H^+]{\text{① } NaBH_4}$$ ✗

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH\,/\,OR\,/\,\ddot{N}H_2 \xrightarrow[\text{(ii) } H_2O\,/\,H^+]{\text{(i) } NaBH_4} \text{X}$$

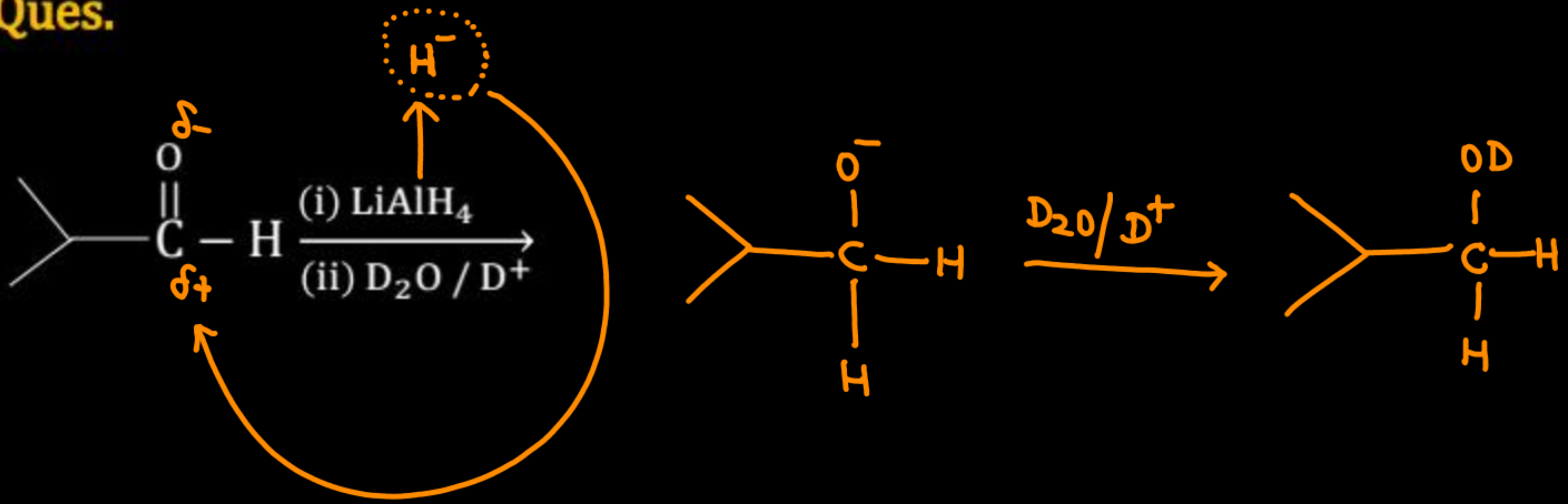
Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{H_2\,/\,Pd\,/\,Pt\,/\,Ni} \text{X}$$

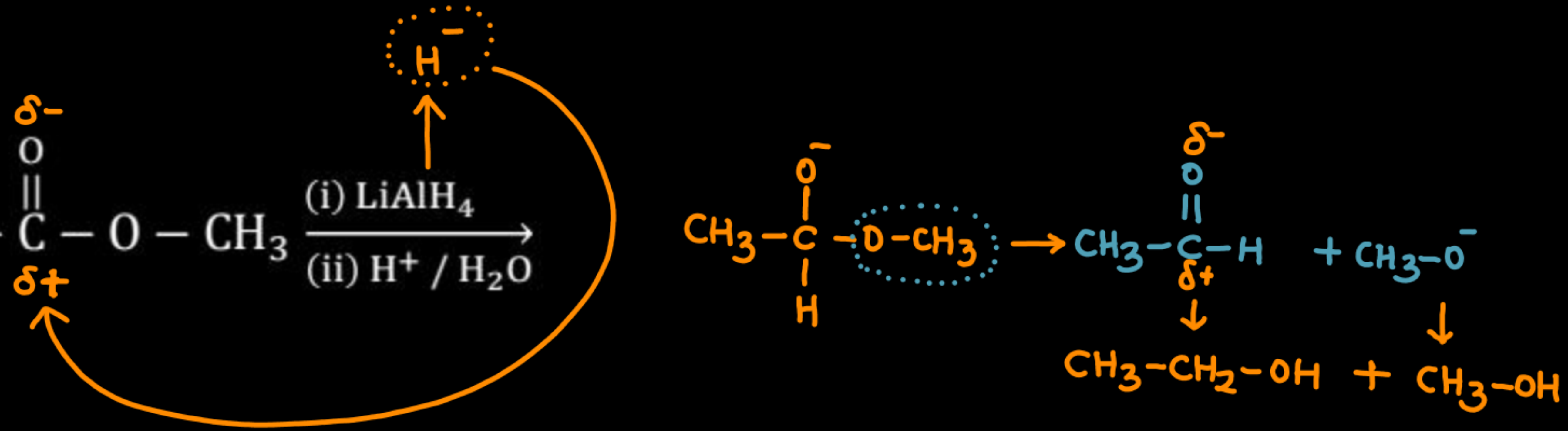
Ques.

$$R-\overset{\overset{\displaystyle O}{||}}{C}-Cl\,/\,OR\,/\,\ddot{N}H_2 \xrightarrow{H_2\,/\,Pd\,/\,Pt\,/\,Ni}$$

Ques.

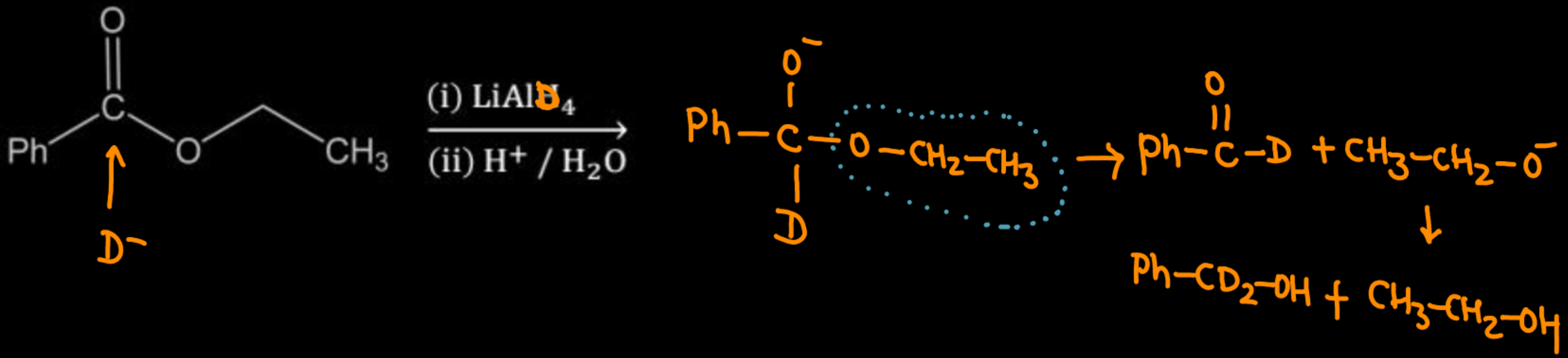


Ques.



CH3 – C – O – CH3
(i) LiAlH4
(ii) H+ / H2O
δ-
δ+
CH3–C–O–CH3
CH3–C–H
+ CH3–O
CH3–CH2–OH + CH3–OH

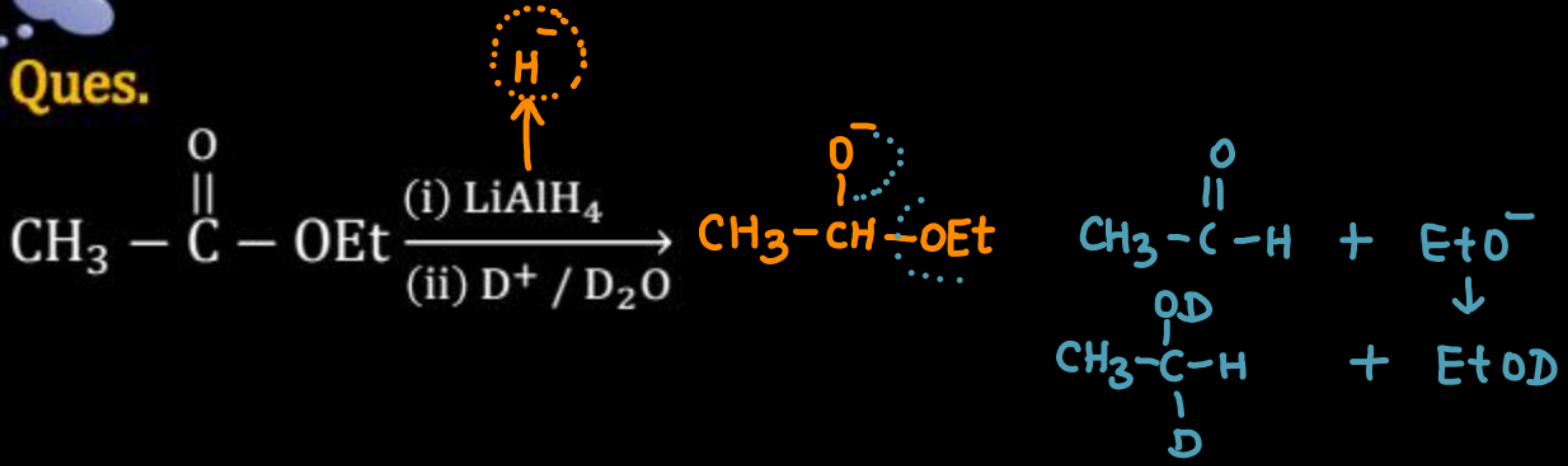
Ques.



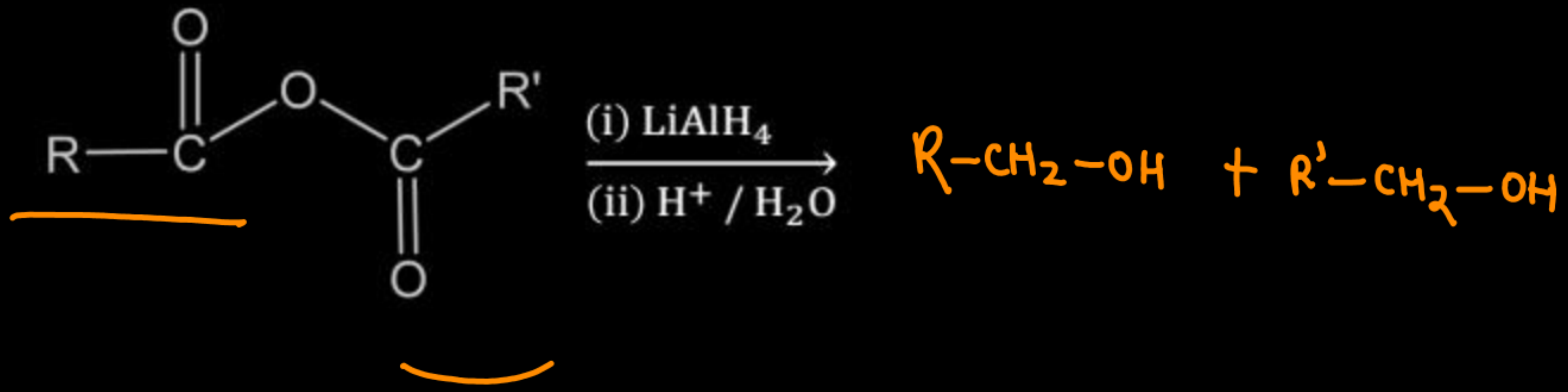
Ph
O
CH3
(i) LiAlD4
(ii) H+ / H2O
D
Ph–C–O–CH2–CH3
Ph–C–D + CH3–CH2–O
Ph–CD2–OH + CH3–CH2–OH



Ques.


CH3 – C – OEt
(i) LiAlH4
(ii) D+ / D2O
H
CH3–CH–OEt
O
CH3 – C – H + EtO
OD
CH3–C–H + EtOD
D

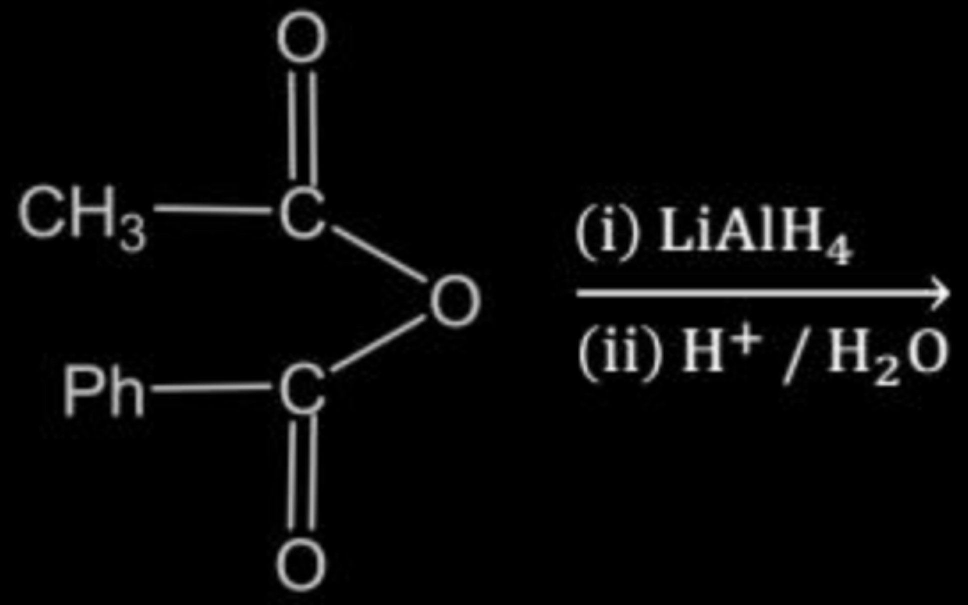
HW **Ques.**


R
O
C
R'
(i) LiAlH4
(ii) H+ / H2O
R–CH2–OH + R'–CH2–OH

Ques.

$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } LiAlH_4} CH_3-\underset{H}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-NH_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-H + NH_3 \longrightarrow CH_3-CH_2-OH + NH_3$$

Ques.



$CH_3-CH_2-OH + Ph-CH_2-OH$



Ques.

$$CH_2 = CH - CH_2 - \overset{\overset{\large O}{||}}{C} - CH_3 \xrightarrow{LiAlH_4} CH_2 = CH - CH_2 - \overset{\overset{\large OH}{|}}{CH} - CH_3$$

Ques.

$$CH_2 = CH - CH_2 - \overset{\overset{\large O}{||}}{C} - CH_3 \xrightarrow{NaBH_4} CH_2 = CH - CH_2 - \overset{\overset{\large OH}{|}}{CH} - CH_3$$

Ques.

$$CH_2 = CH - CH_2 - \overset{\overset{\large O}{||}}{C} - CH_2 \xrightarrow{H_2 / Pd, Pt, Ni} CH_3 - CH_2 - CH_2 - \overset{\overset{\large OH}{|}}{CH} - CH_3$$



$NaBH_4 \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl,\ R-\overset{O}{\overset{\|}{C}}-H,\ R-\overset{O}{\overset{\|}{C}}-R'$

Functional Group	Products	$LiAlH_4$	$NaBH_4$	H_2/Ni, Pd, Pt
$R-\overset{O}{\overset{\|}{C}}-H$	$R-CH_2-OH$	✓	✓	✓
$R_1-\overset{O}{\overset{\|}{C}}-R_2$	$R_1-\overset{OH}{\overset{\vert}{C}H}-R_2$	✓	✓	✓
$R-\overset{O}{\overset{\|}{C}}-Cl$	$R-CH_2OH + HCl$	✓	✓	✓
$R-\overset{O}{\overset{\|}{C}}-O-R'$	$R-CH_2OH + R'OH$	✓	✗	✓



Functional Group	Products	$LiAlH_4$	$NaBH_4$	$H_2/Ni, Pd, Pt$
$R-\overset{O}{\overset{\|\|}{C}}-O-\overset{O}{\overset{\|\|}{C}}-R'$	$R-CH_2OH + R'CH_2OH$	✓	✗	✓
$R-\overset{O}{\overset{\|\|}{C}}-\ddot{N}H_2$	$R-CH_2-OH + NH_3$	✓	✗	✓
$R-\overset{O}{\overset{\|\|}{C}}-OH$	$R-CH_2-OH + H_2O$	✓	✗	✗
$R-CH=CH_2$	$R-CH_2-CH_3$	✗	✗	✓

Chemical Properties of Alcohol

R-O-H behaves as electrophile as well as nucleophile.

$$R-\ddot{\underset{..}{O}}-H + E^+$$

Nucleophile

$R-O^-$ H^+

$$R-\ddot{\underset{..}{O}}-H \xrightarrow{H^+} R-\overset{\oplus}{O}H_2 \longrightarrow \overset{\oplus}{R} + H_2O$$

Electrophile

R^+ $+ H_2O$

Chemical Reaction of Alcohol



→ Reaction involving breaking of OH bond :-

(i) Reaction with metal → H_2 Release

(ii) Acidic nature of alcohol → H^+ Remove → Anion Form
↓
Stable anion
↓
More acidic
↓
−M, −H, −I

(i) $CH_3-OH + Na/K/Ca \longrightarrow CH_3-O^- + \frac{1}{2}H_2\uparrow$

alcohol — acidic (H)

active metal — Basic

$CH_3-CH(CH_3)-OH + Ca \longrightarrow (CH_3-CH(CH_3)-O^-)_2Ca + H_2$

$CH_3-C(CH_3)_2-OH + Al \longrightarrow (CH_3-C(CH_3)_2-O^-)_3Al + \frac{3}{2}H_2$

(ii) $R-CH_2-OH$ R_2CH-OH R_3C-OH

acidic nature → a > b > c

+I ↑ acidic ↓

Chemical Reaction of Alcohol



→ Reaction involving breaking of OH bond :-

(i) Reaction with metal → H_2 Release

(ii) Acidic nature of alcohol → H^+ Remove → Anion Form → Stable anion → More acidic → −M, −H, −I

(iii) Esterification Reaction
↳ Formation of Ester
↓
alcohol + acid
or
alcohol + acid derivative

(iv) Reaction with aldehyde/ketone.

(v) Reaction with Grignard (PPCH)

O_2N-CH_2-OH $\quad$ $Ph-CH_2-OH$ $\quad$ $F-CH_2-OH$

acidic → a > c > b

(iii)

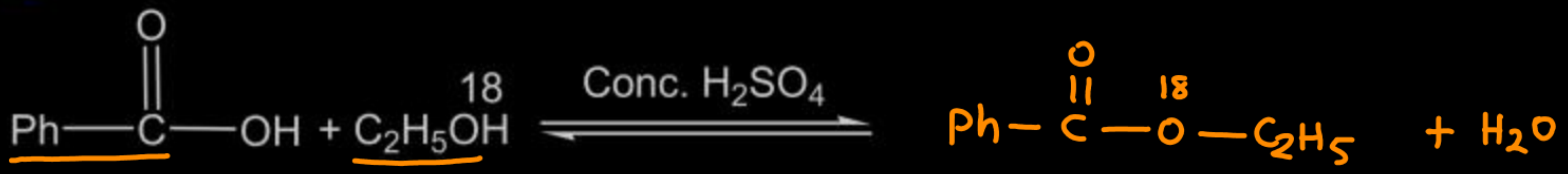
$$\underbrace{R_1-OH}_{\text{alcohol}} + \underbrace{R_2-\overset{O}{\overset{\|}{C}}-O-H}_{\text{acid}} \rightarrow \underbrace{R_2-\overset{O}{\overset{\|}{C}}-O-R_1}_{\text{Ester}} + H_2O$$

$$\underline{R_1-OH} + \underline{R_2-\overset{O}{\overset{\|}{C}}-Cl} \longrightarrow R_2-\overset{O}{\overset{\|}{C}}-O-R_1 + HCl$$

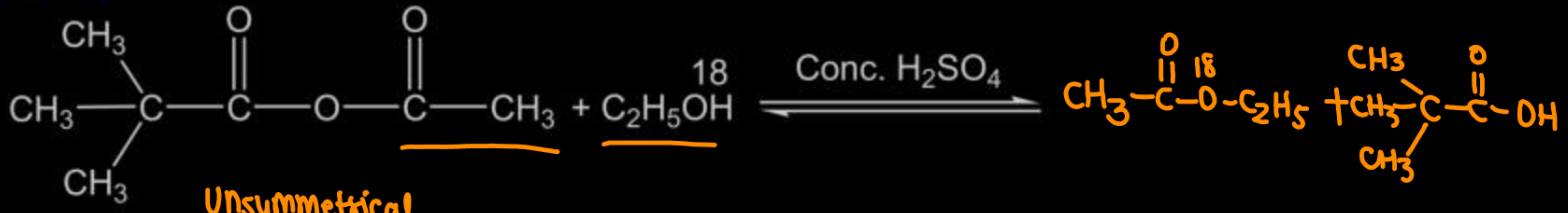
$$\underline{R_1-OH} + \underline{R_2-\overset{O}{\overset{\|}{C}}}-O-\overset{O}{\overset{\|}{C}}-R_2 \longrightarrow \underbrace{R_2-\overset{O}{\overset{\|}{C}}-O-R_1}_{\text{Ester}} + \underbrace{R_2-\overset{O}{\overset{\|}{C}}-OH}_{\text{acid}}$$

Examples of Esterification Reaction:

Ques.



Ques.



Unsymmetrical anhydride

↓

Small Side → Ester



Ques.

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + C_2H_5\overset{*}{O}H \xrightarrow{\text{base}} CH_3-\overset{\overset{O}{\|}}{C}-\overset{*}{O}-C_2H_5$$

Examples of Acetylation, Alkylation and Benzoylation:

Ques.

$$CH_3-\overset{\overset{O}{||}}{C}-OH + CH_3OH \xrightleftharpoons{H^+} CH_3-\overset{\overset{O}{||}}{C}-O-CH_3$$

Ques.

$$R-OH + Na \longrightarrow R-\bar{O} + H_2\uparrow$$

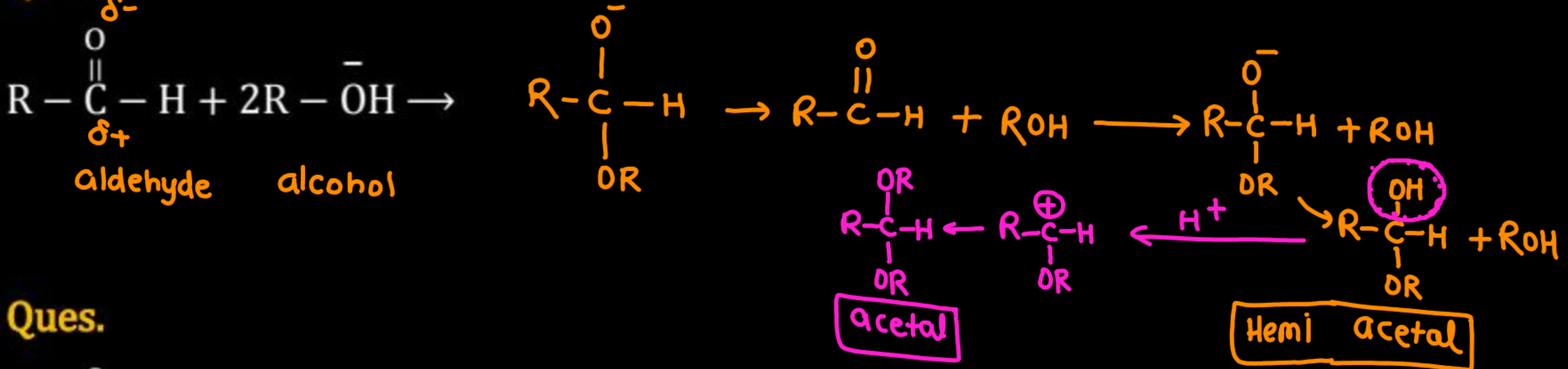
Ques.

$$Ph-\overset{\overset{O}{\|}}{C}-Cl + C_2H_5OH \longrightarrow Ph-\overset{\overset{O}{\|}}{C}-O-C_2H_5$$

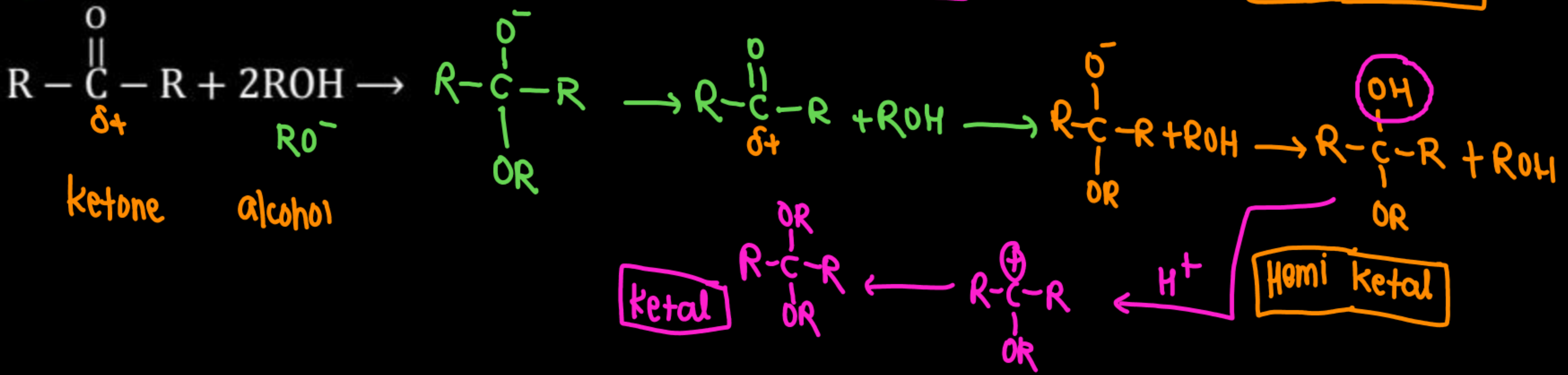
Ester

Reaction with aldehyde/ketone:

Ques.



Ques.



Reaction with Grignard:

General Reaction:

Ques.

$$R' - Mg - X + R - O - H \longrightarrow R' - H + Mg\begin{smallmatrix} X \\ OR \end{smallmatrix}$$

R'^{-}

Ques.

$$CH_3 - MgBr + CH_3 - CH_2 - CH_2 - OH \longrightarrow CH_4 + Mg\begin{smallmatrix} Br \\ O-CH_2-CH_2-CH_3 \end{smallmatrix}$$

CH_3^{-}

alkane

Reaction involving cleavage of R–O bond

1. Lucas Test PPCH · → HCl + anhy $ZnCl_2$
2. Reaction with PCl_5 & PCl_3 · PPCH → adds 'cl'
3. Darzen Reaction ($SOCl_2$) PPCH → Good yield $SO_2\uparrow$ + $HCl\uparrow$
4. Dehydration Reaction (PPCH) → Carbocation → Rarrange (H_2O Remove)
5. ✓ oxidation of alcohol
6. ✓ pinnacole pinnacolone Rearrangement
7. ✓ Test of alcohol



Reaction involving cleavage of R—O bond

① Reaction with HCl & $ZnCl_2$ $\xrightarrow[\text{anhy } ZnCl_2]{\text{Conc HCl}}$ Lucas Reagent → Turbidity

② Reaction with H^+ (Conc H_2SO_4) $\xrightarrow{\text{Dehydration}}$ Carbocation → Rearrange → Alkene

③ Reaction with PCl_5, PCl_3, $SOCl_2$
(darzen Rxn)

Reaction with Hydrogen halide:

General Reaction:

Ques.

$$R-\ddot{O}-H + H^{+}X^{-} \longrightarrow R-X$$

(Turbidity)

Ques.

1° alc. $R-CH_2OH + \text{Conc. HCl} \xrightarrow[\Delta]{ZnCl_2}$ Slow Reaction

$R-CH_2-Cl$

30min

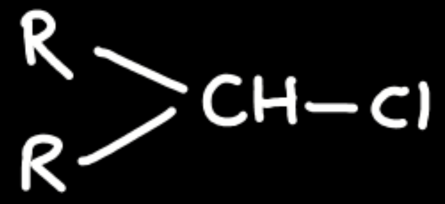
Turbidity

(Heat)

Ques.

2° alc. $R_2CHOH + \text{Conc. HCl} \xrightarrow{ZnCl_2}$ Fast Reaction

R_2CHCl

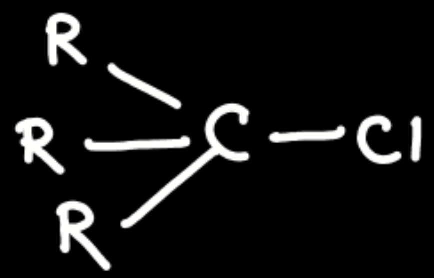


5 min Turbidity

Ques.

3° alc $R_3COH + \text{COnc. HCl} \xrightarrow{ZnCl_2}$ Fastest Reaction

R_3CCl



Immediate Turbidity



Ques. Which of the following do not produce turbidity at room temperature?

(i) 1° Alcohol (ii) 2° Alcohol (iii) 3° Alcohol (iv) N.O.T

Reaction with PCl_5, PCl_3, $SOCl_2$:

Ques.

$R - OH + PCl_5 \longrightarrow$ $R-Cl + H-Cl + POCl_3$

$\downarrow$

$PCl_3 + Cl_2$



Ques.

$R - OH + PCl_3 \longrightarrow$ $R-Cl + H_3PO_3$

Ques.

$R - OH + SOCl_2 \xrightarrow[\text{reaction}]{\text{darzen}}$ $R-Cl + \underset{(g)}{H-Cl}\uparrow + \underset{(g)}{SO_2}\uparrow$ (good yield Reaction) (products are gases escape out from reaction)

↓ good yield (below R-Cl)



Protonation of alcohol

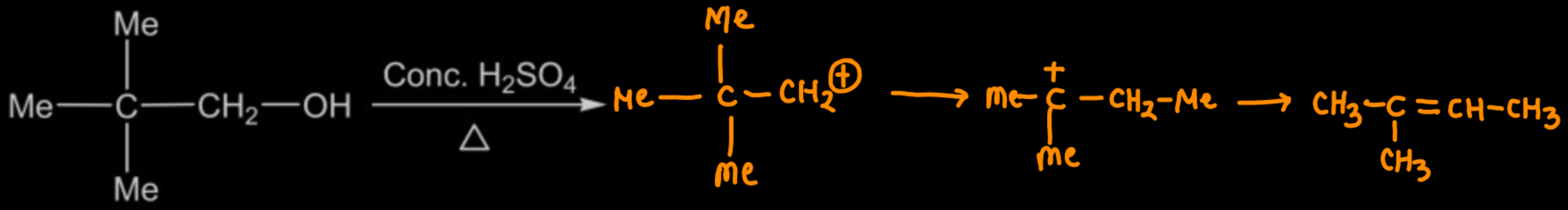
$$CH_3-CH_2-CH_2-OH \xrightarrow{H^+} CH_3-CH_2-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{\oplus}{C}H-CH_3 \rightarrow CH_2=CH-CH_3$$

Step 1 → Protonation of Alcohol

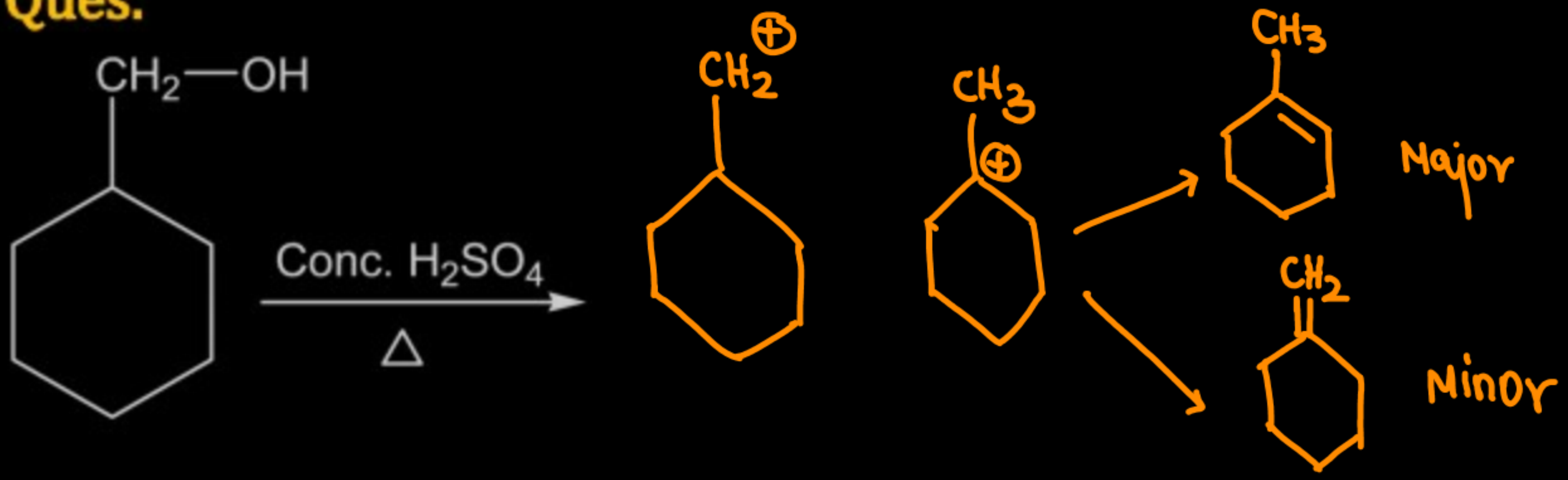
Step 2 → alkene formation

Examples of reactivity of order of dehydration:

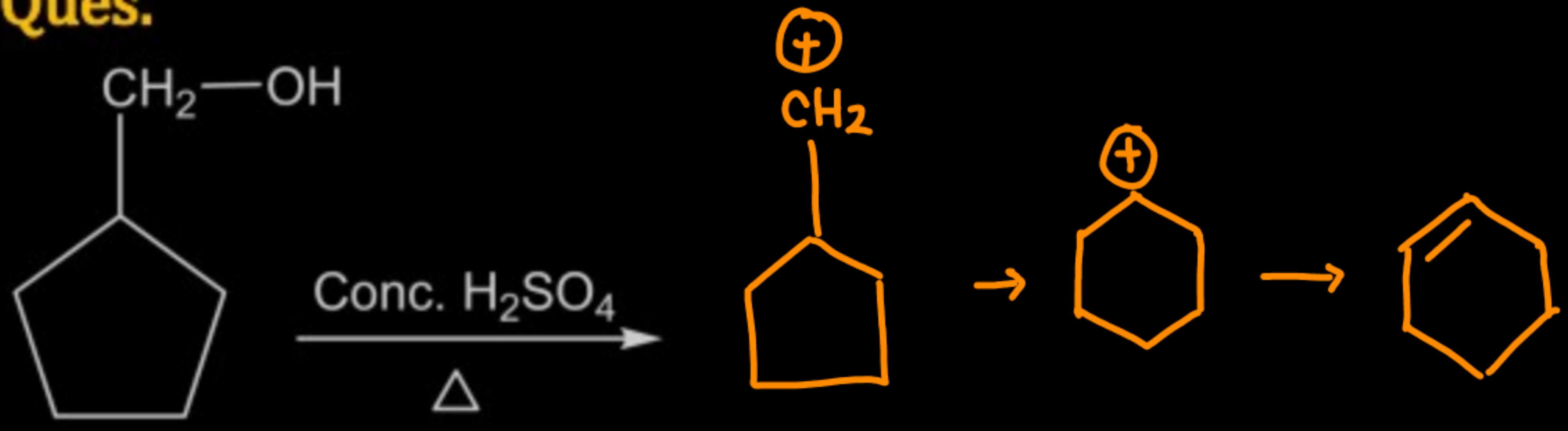
Ques.



Ques.



Ques.



$C_2H_5OH + H_2SO_4$

- $\xrightarrow{100°C}$ $C_2H_5-HSO_4$ -vecharge Substitution
- $\xrightarrow{140°C}$ $C_2H_5-O-C_2H_5$ ether
- $\xrightarrow{170°C}$ $CH_2=CH_2$ alkene

Oxidation of Alcohol

(i) $CH_3-CH_2-OH \xrightarrow[H^+/K_2Cr_2O_7]{H^+/KMnO_4 \text{ or}} CH_3-\overset{\overset{O}{||}}{C}-H \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-OH$

alcohol

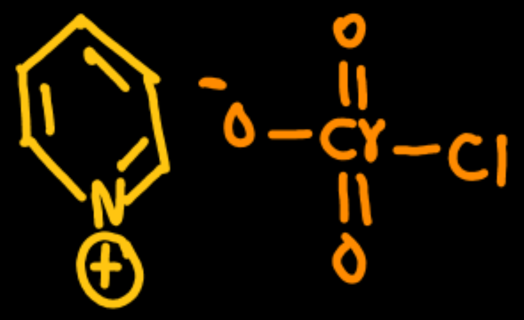
(strong oxidising agent)

(ii) if we want aldehyde then use either CrO_3 or PCC.

$CH_3-CH_2-OH \xrightarrow{CrO_3} CH_3-\overset{\overset{O}{||}}{C}-H$

alcohol → aldehyde

$CH_3-CH_2-OH \xrightarrow[\text{Pyridinium chlorochromate}]{PCC} CH_3-\overset{\overset{O}{||}}{C}-H$



Oxidation of Alcohol:

Ques.

$$R-\underset{}{\overset{OH}{\overset{|}{C}}}H-R' \xrightarrow[H^+/\,K_2Cr_2O_7]{H^+\,/\,KMnO_4} R-\overset{O}{\overset{\|}{C}}-R' \quad \text{(ketone)}$$

Ques.

$$R-\overset{OH}{\overset{|}{C}}H-R' \xrightarrow{CrO_3} R-\overset{O}{\overset{\|}{C}}-R' \quad \text{(ketone)}$$

Ques.

$$R-\overset{\displaystyle R''}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-R' \longrightarrow$$ no reaction

Ques.

$$R-\overset{\displaystyle R''}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-R' \xrightarrow[\text{H}^+/\ \text{K}_2\text{Cr}_2\text{O}_7 \text{ and high temp.}]{\text{H}^+/\ \text{KMnO}_4 \text{ or}}$$ no reaction

Ques.

$$1^\circ \text{ Alcohol} \xrightarrow[H^+/\,K_2Cr_2O_7]{H^+\,/\,KMnO_4} \text{acid}$$

Ques.

$$1^\circ \text{ Alcohol} \xrightarrow{CrO_3} \text{aldehyde}$$

Ques.

$$1° \text{ Alcohol} \xrightarrow{PCC} \text{aldehyde}$$

Ques.

$$2° \text{ Alcohol} \xrightarrow{H^+ / KMnO_4} \text{ketone}$$

Ques.

$$2^\circ \text{ Alcohol} \xrightarrow{CrO_3} \text{ketone}$$

Ques.

$$3^\circ \text{ Alcohol} \longrightarrow \quad X$$

Ques.

$$3^\circ \text{ Alcohol} \xrightarrow[H^+ / K_2Cr_2O_7 / \Delta]{H^+ / KMnO_4} \times$$

$$\xrightarrow{CrO_3} \times$$

$$\xrightarrow{PCC} \times$$

$$1^\circ \text{ alcohol} \xrightarrow[H^+/K_2Cr_2O_7]{H^+/KMnO_4 \text{ or}} \text{acid}$$

$$2^\circ \text{ alcohol} \xrightarrow{''} \text{Ketone}$$

$$3^\circ \text{ alcohol} \xrightarrow{''} \times$$

$$1^\circ \text{ alcohol} \xrightarrow{CrO_3} \text{aldehyde}$$

$$2^\circ \text{ alcohol} \xrightarrow{CrO_3} \text{ketone}$$

$$3^\circ \text{ alcohol} \xrightarrow{CrO_3} \text{No Reaction}$$

$$1^\circ \text{ alcohol} \xrightarrow{PCC} \text{aldehyde}$$

$$2^\circ \text{ alcohol} \xrightarrow{PCC} \text{Ketone}$$

$$3^\circ \text{ alcohol} \xrightarrow{PCC} \text{No Reaction}$$

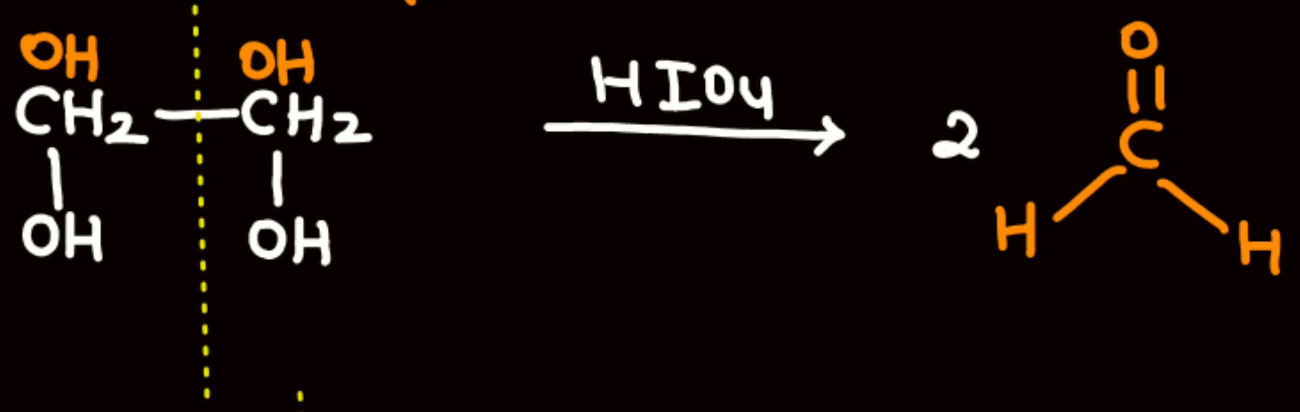
Oxidation with HIO_4

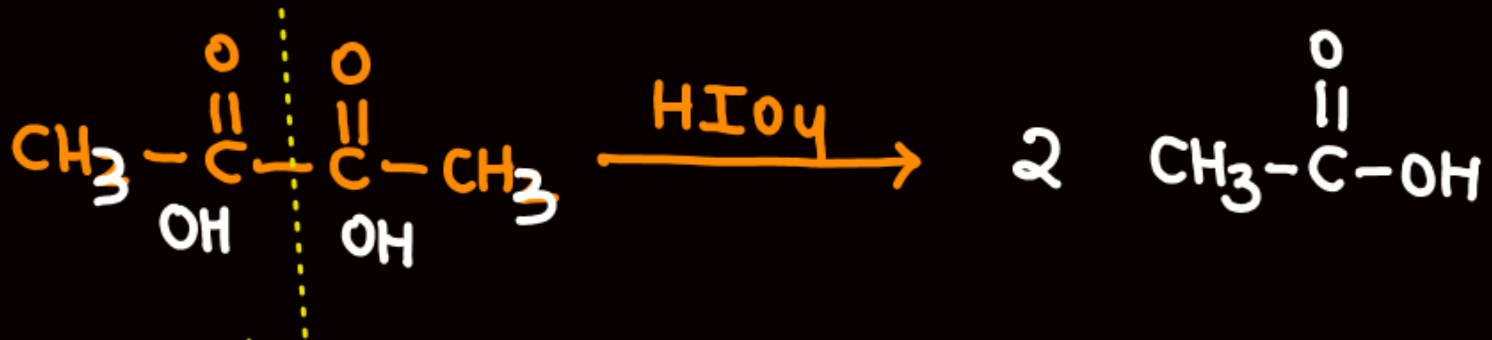
→ Vicinal OH

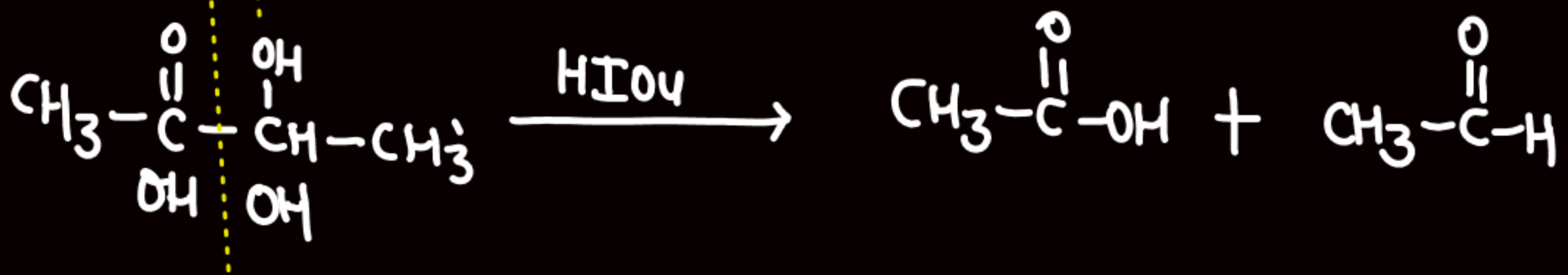
→ Vicinal $>C=O$

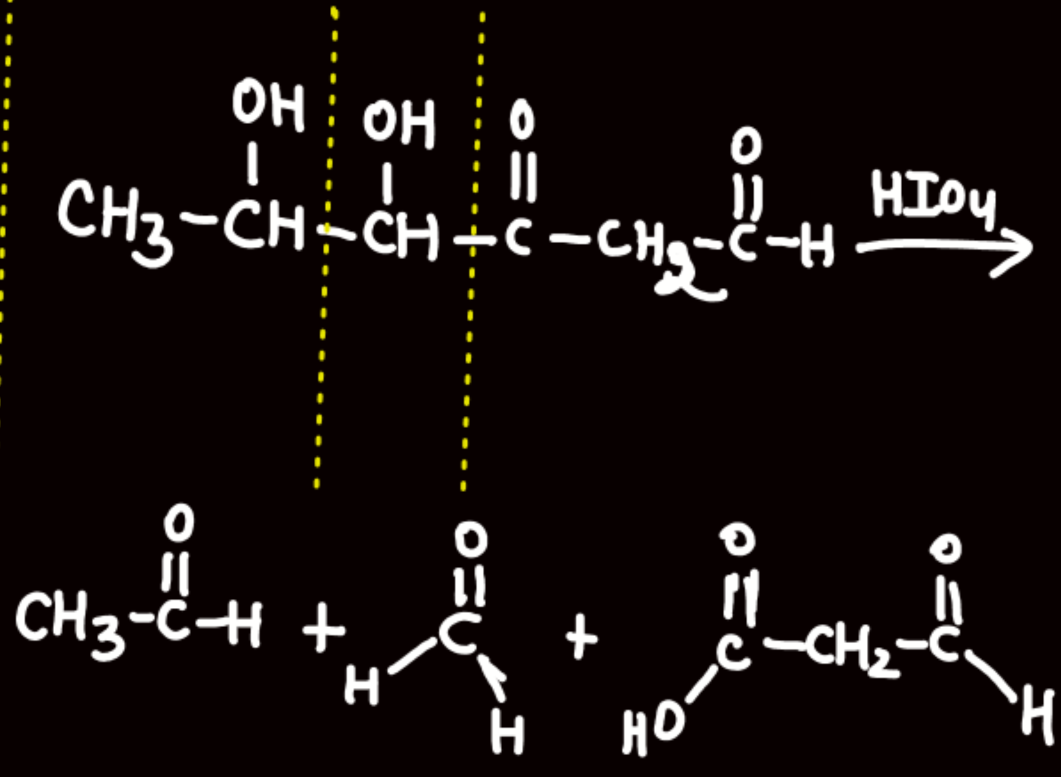
→ Vicinal $>C=O$ and OH

Break the bond & add OH on both Sides.









Test of alcohol

Oxidation with Cu/300°C (Test 1°/2°/3° Alcohol):

Ques.

$$CH_3-CH_2-OH \xrightarrow{Cu\,/\,300°C} CH_3-\overset{\overset{O}{\|}}{C}-H$$

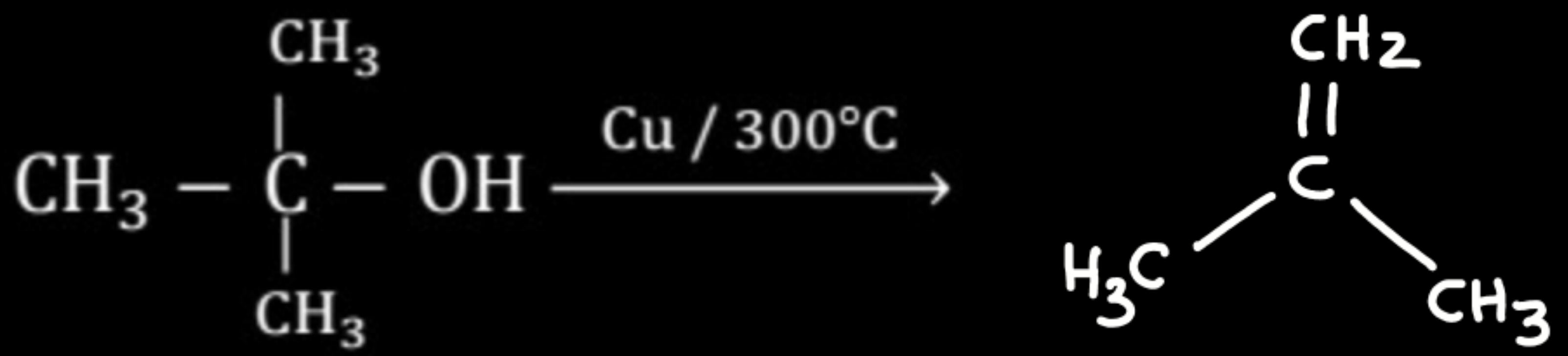
1° alcohol — aldehyde

Ques.

$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu\,/\,300°C} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

2° alcohol — ketone

Ques.



3° alcohol

alkene



(2) Lucas Test ⟶ Conc. $HCl + ZnCl_2$

1° Alcohol ⟶ Turbidity (30 min) (Heat)

2° Alcohol ⟶ Turbidity (5 min)

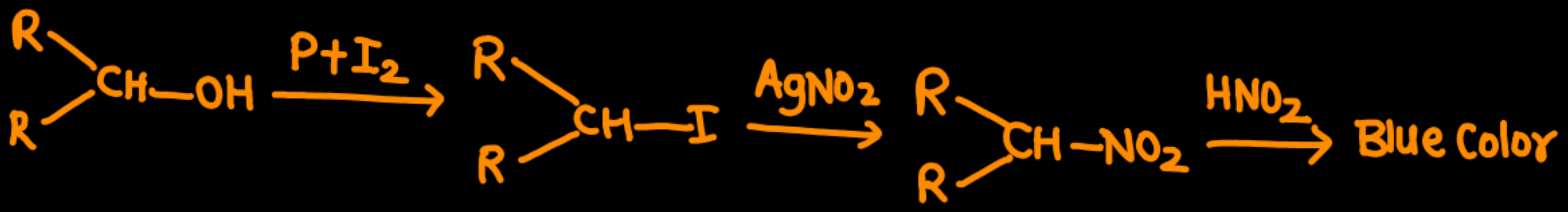
3° Alcohol ⟶ Turbidity (Immediately)

(2) Victor Mayer's Test (Colour test of alcohol) (RBC Test)

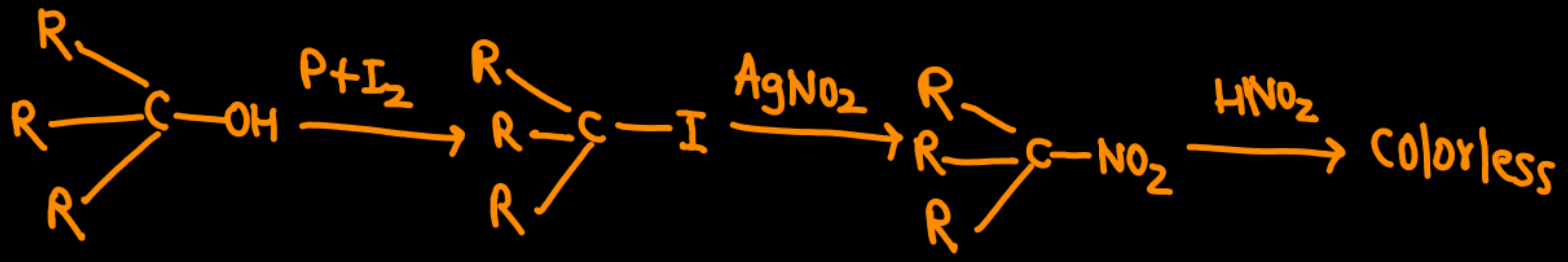
1° Alcohol ⟶ Red color

$$R{-}CH_2{-}OH \xrightarrow{P+I_2} R{-}CH_2{-}I \xrightarrow{AgNO_2} R{-}CH_2{-}NO_2 \xrightarrow{HNO_2} \text{Red Color}$$

2° Alcohol ⟶ Blue color



3° Alcohol ⟶ colorless





(3) Dichromate Test (Only distinguish 3°)

$$1^\circ \text{ Alcohol} \xrightarrow{H^+ \; K_2\overset{+6}{Cr_2}O_7} \text{acid} + Cr^{+3}$$
green Color

$$2^\circ \text{ Alcohol} \xrightarrow{H^+ \; K_2Cr_2O_7} \text{ketone} + Cr^{+3}$$
green color

$$3^\circ \text{ Alcohol} \xrightarrow{H^+ \; K_2Cr_2O_7} \text{No Reaction}$$

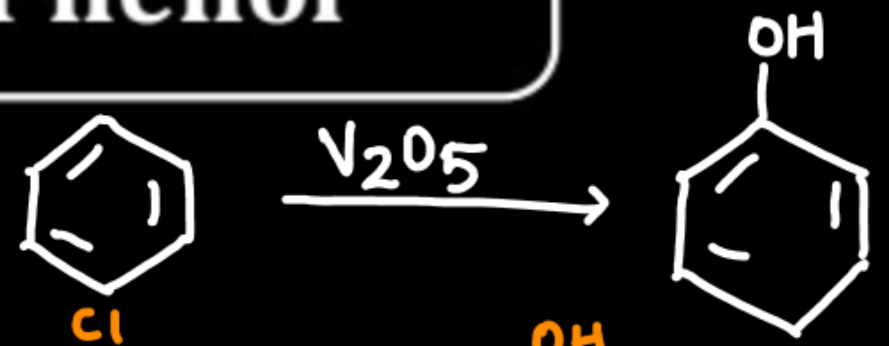


Phenol



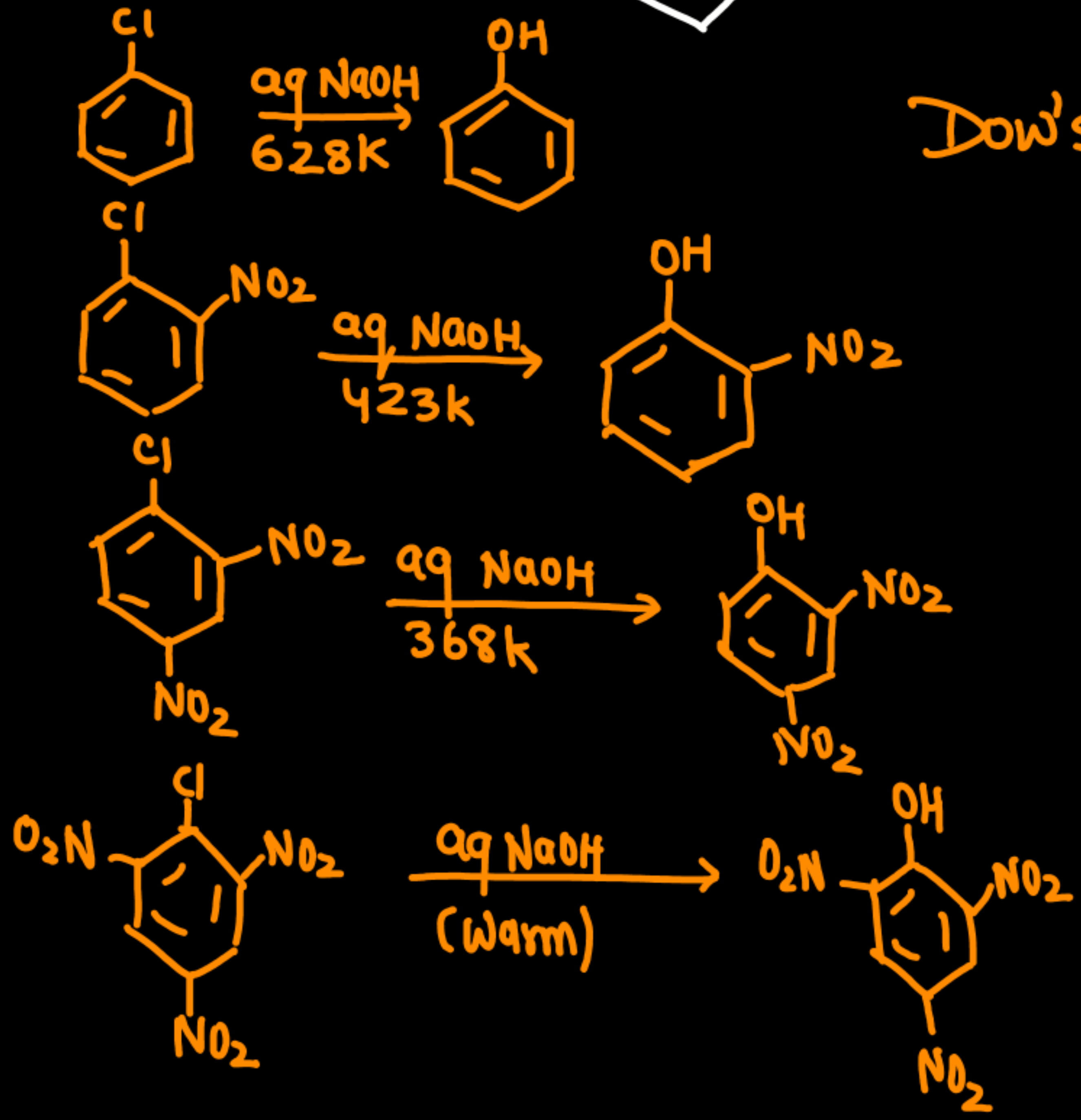
1. Benzene → Phenol
2. ChloroBenzene → Phenol
3. Benzenesulphonic acid
4. Benzene diazonium Salt
5. Cummene
6. Salicylic acid
7. Grignard

(i)



oxidation

(ii)

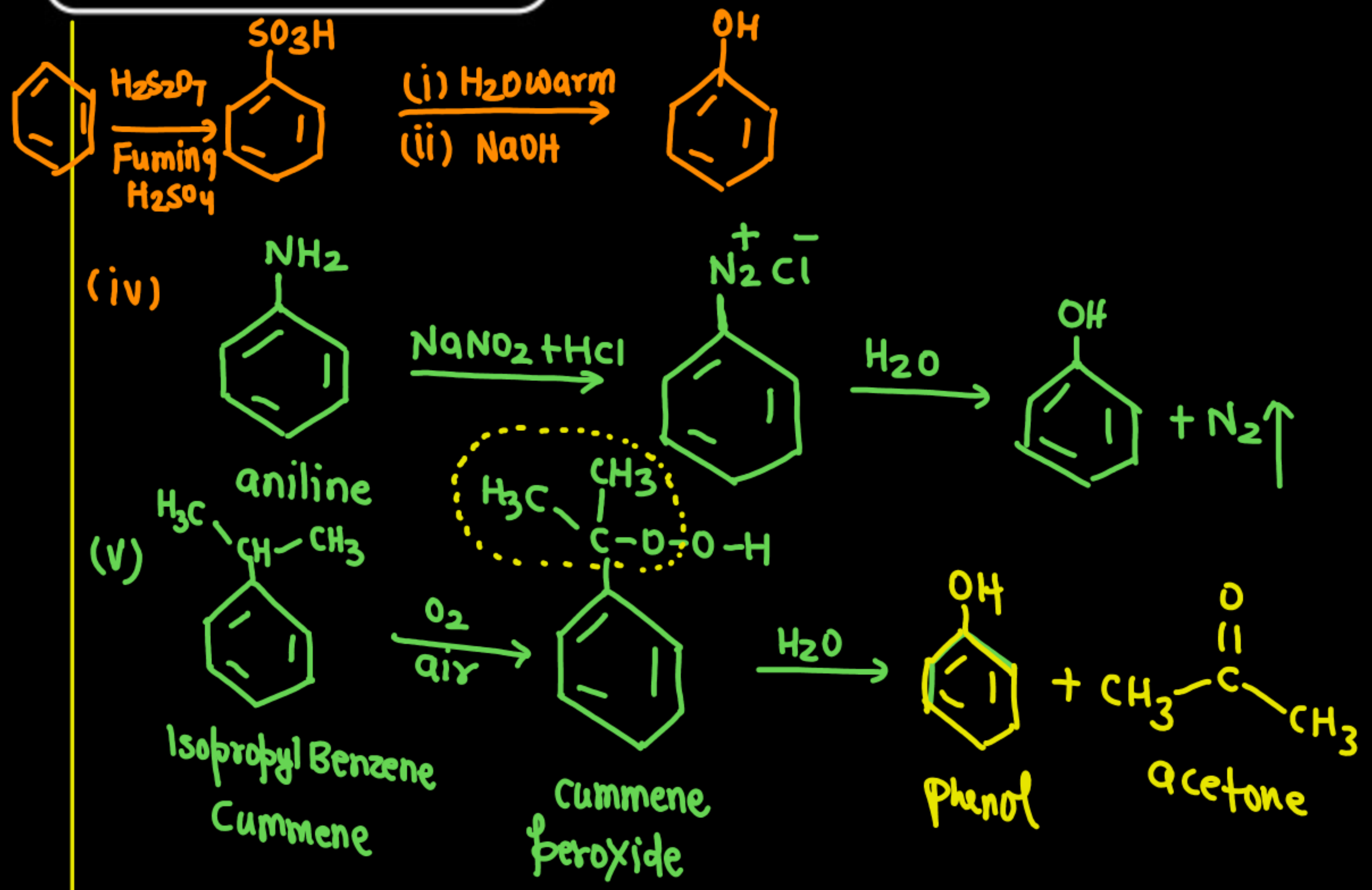


Dow's Process

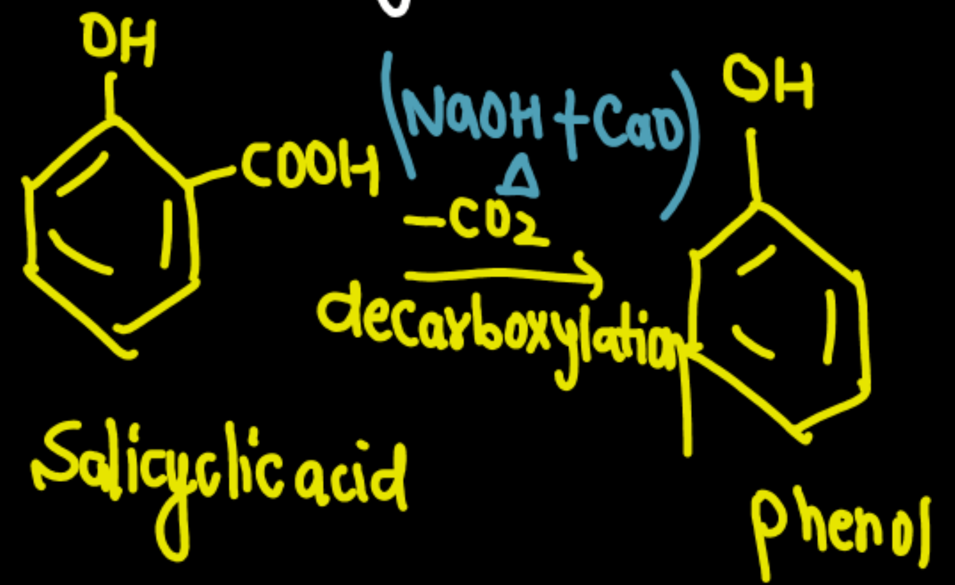
Picric Acid

Phenol

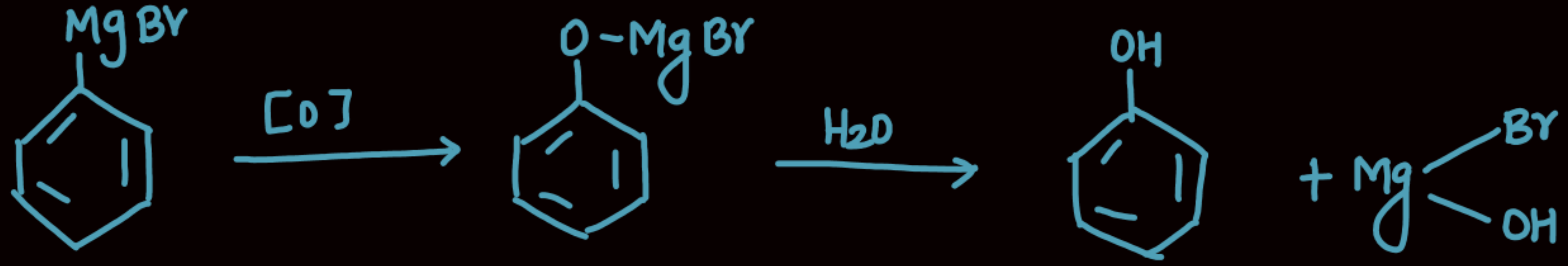
1. Benzene → Phenol
2. ChloroBenzene → Phenol
3. Benzenesulphonic acid
4. Benzene diazonium Salt
5. Cummene *
6. Salicylic acid
7. Grignard



(6)



*

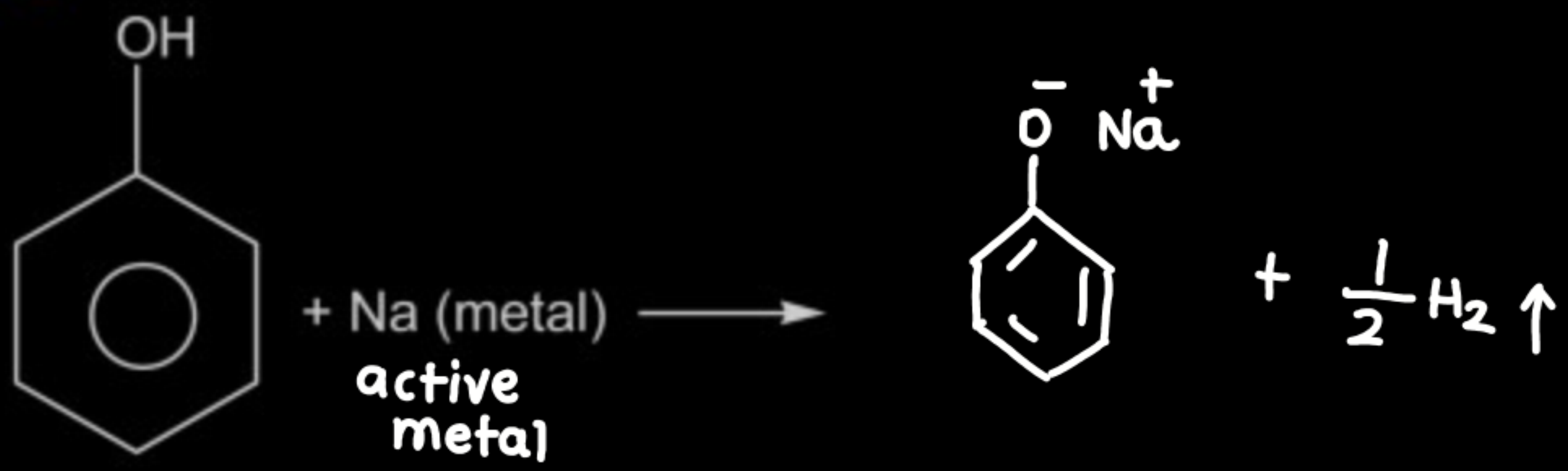


MgBr
[O]
O–MgBr
H2O
OH
+ Mg
Br
OH

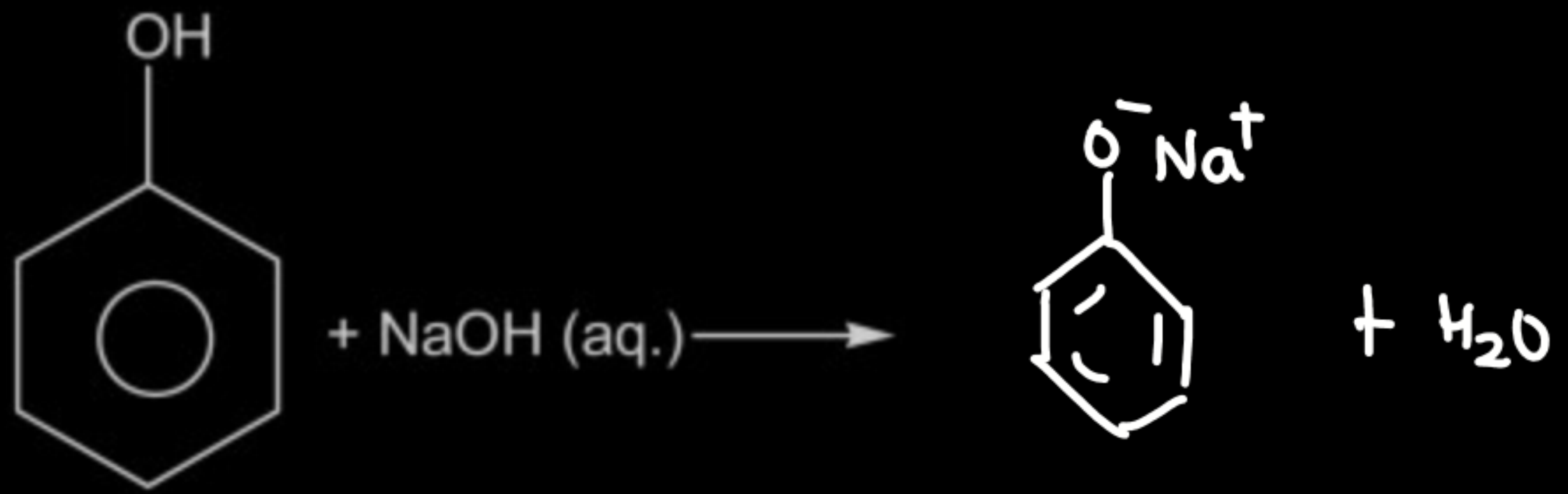
Chemical Reaction of Phenol

Reaction with metal:

Ques.

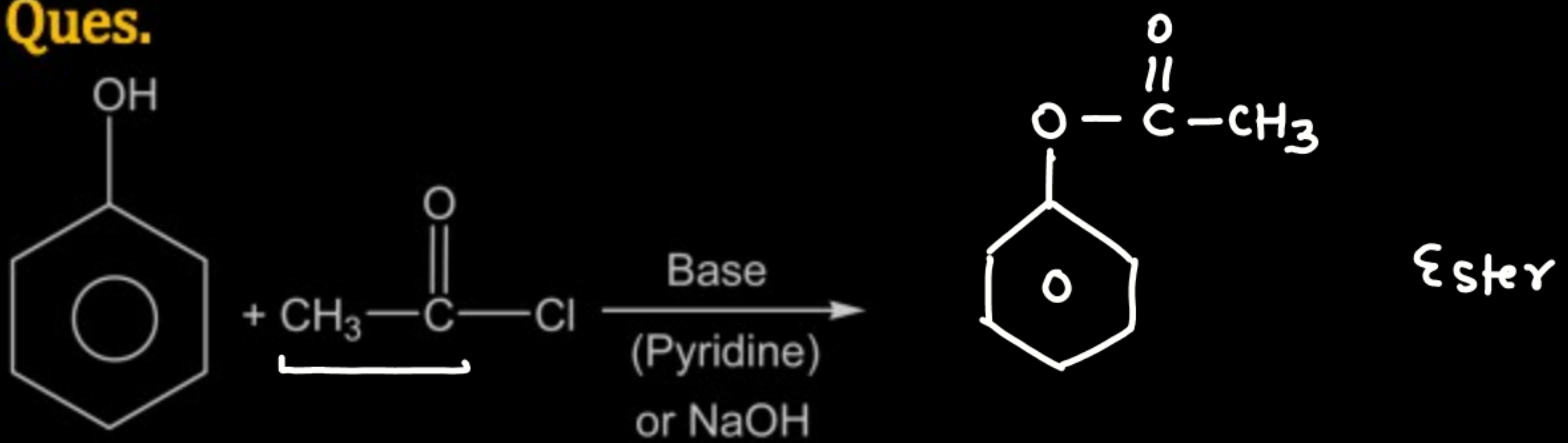


Ques.

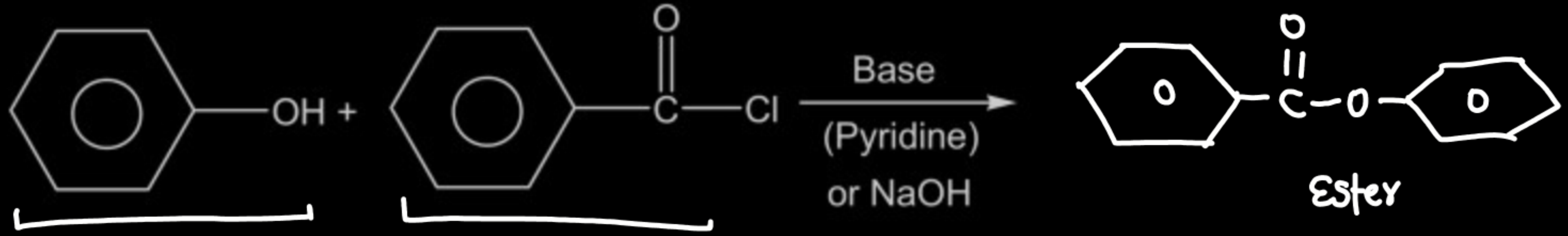


(A) Acetylation

Ques.



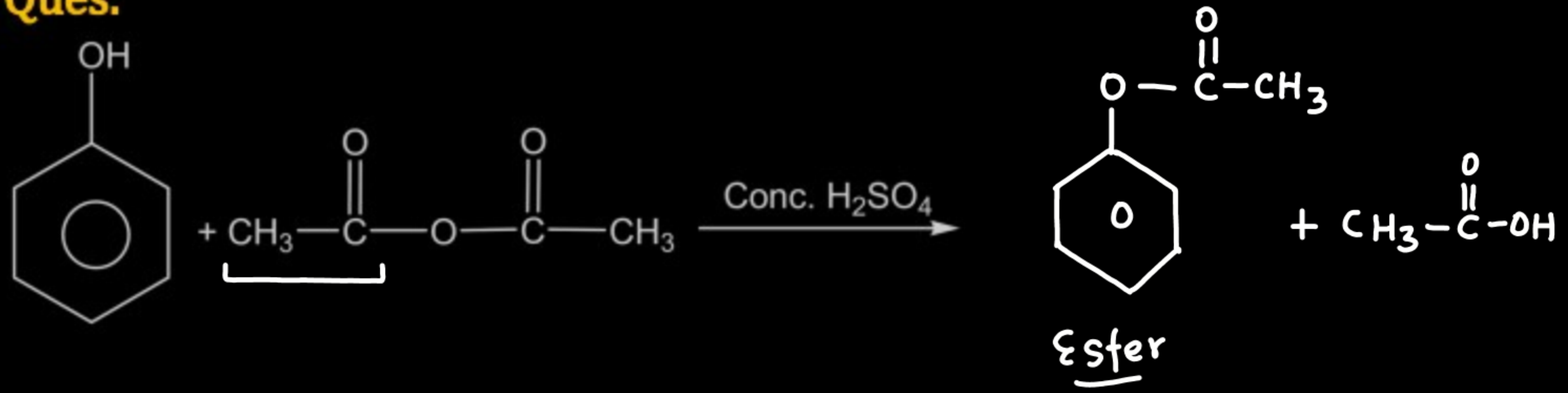
Ques.



Esterification

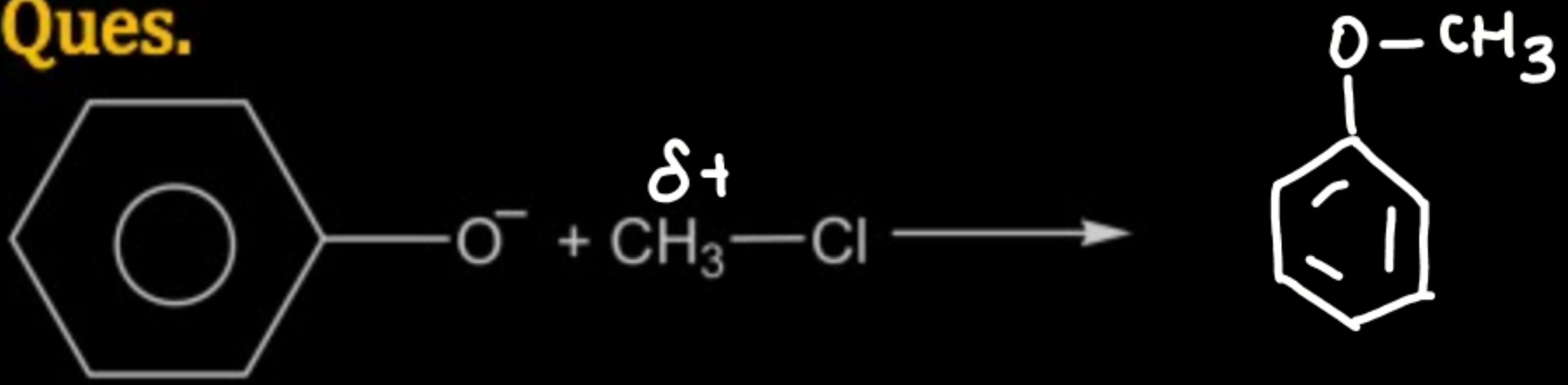
Note: Acetylation of salicylic acid produces aspirin

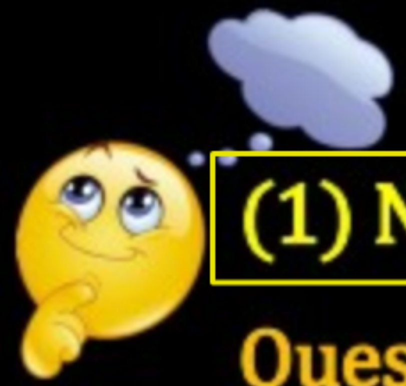
Ques.



(B) Alkylation

Ques.

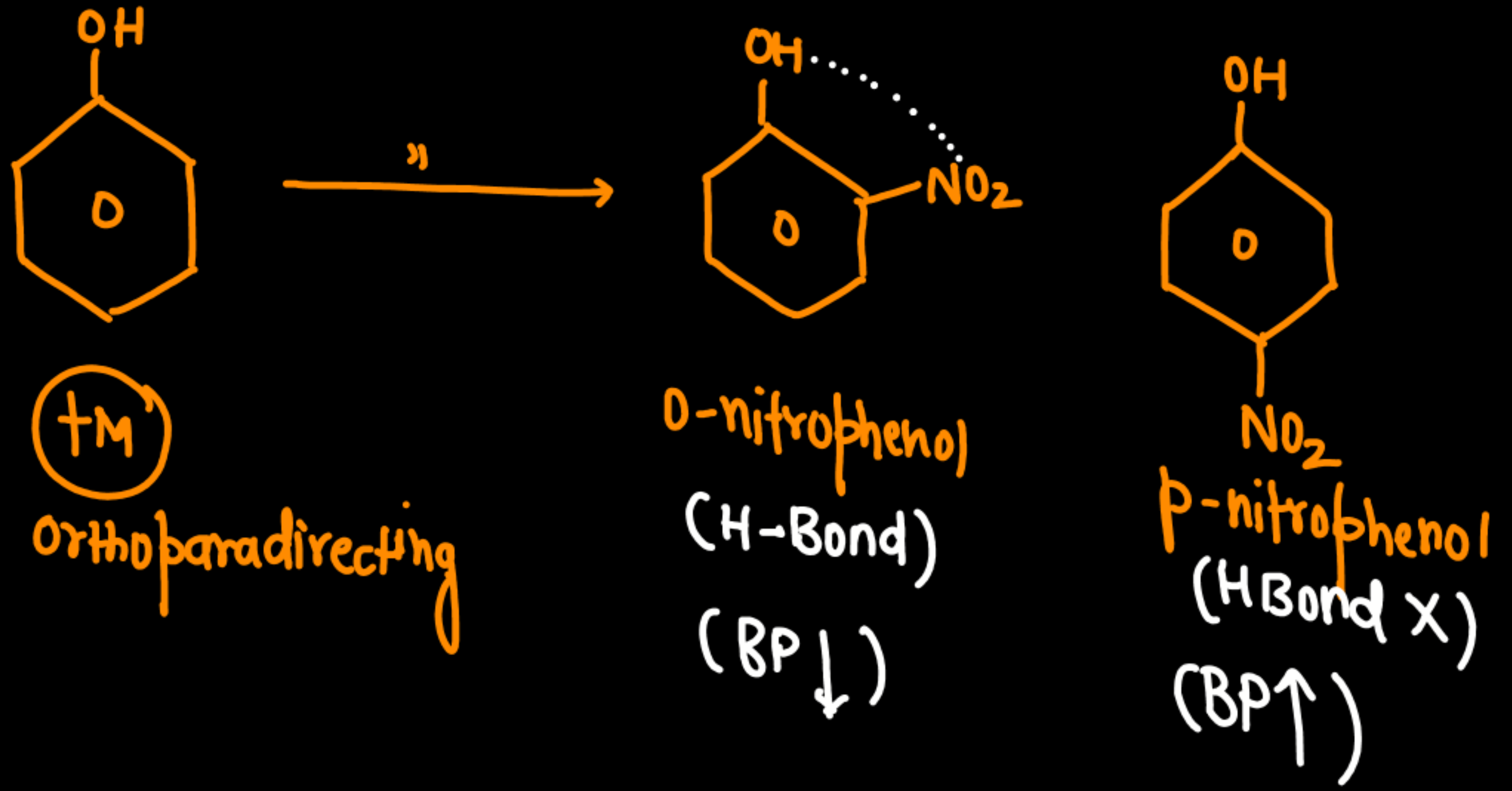




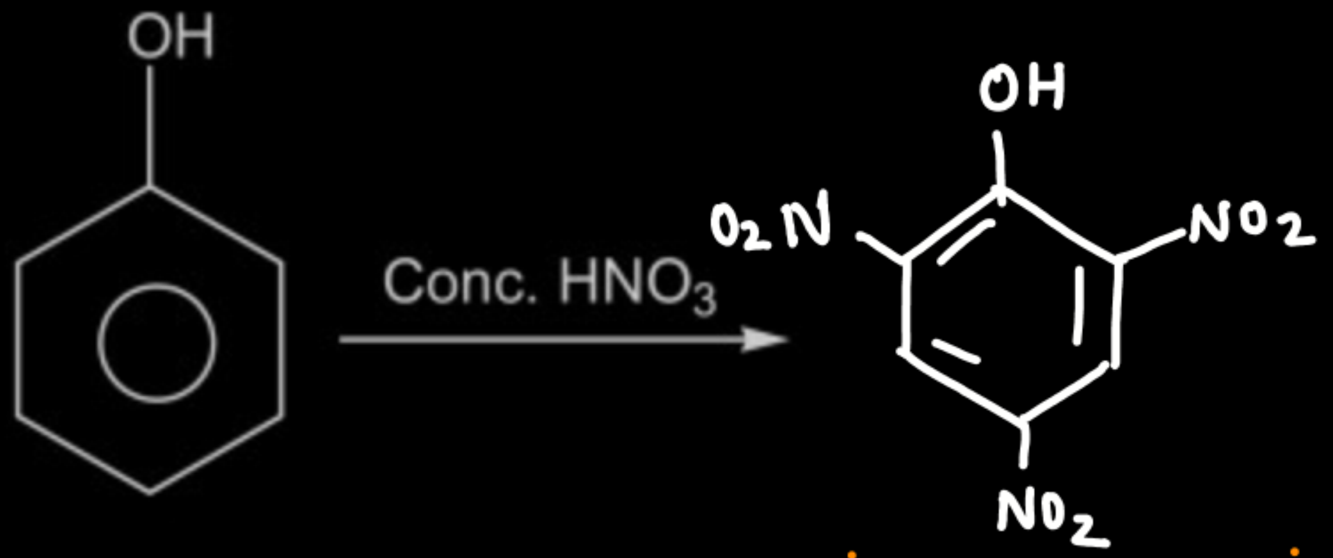
(1) Nitration:

Ques.





Ques.

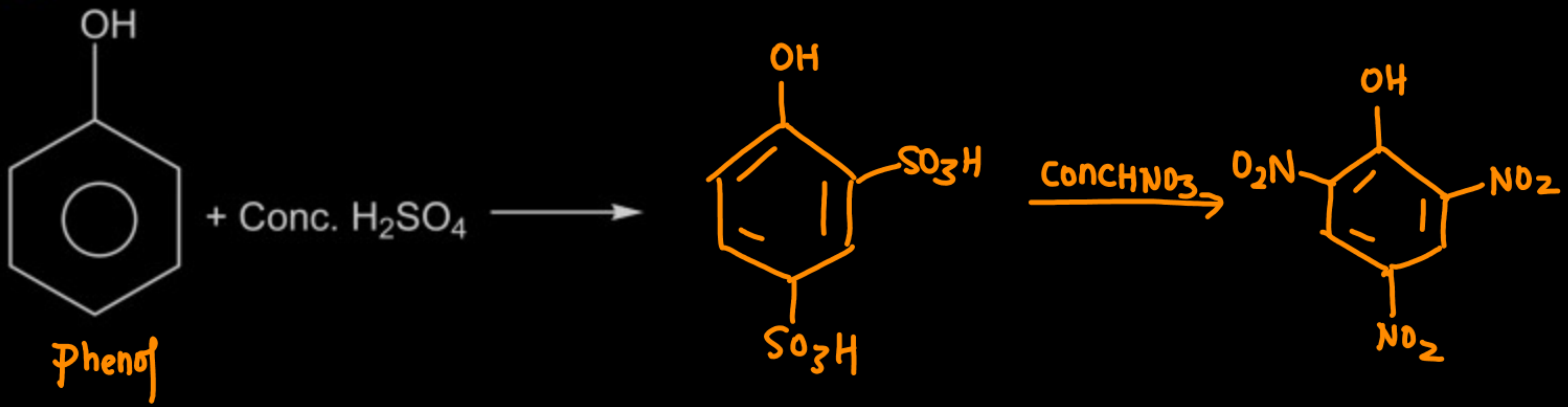


Picric acid

2,4,6-trinitrophenol

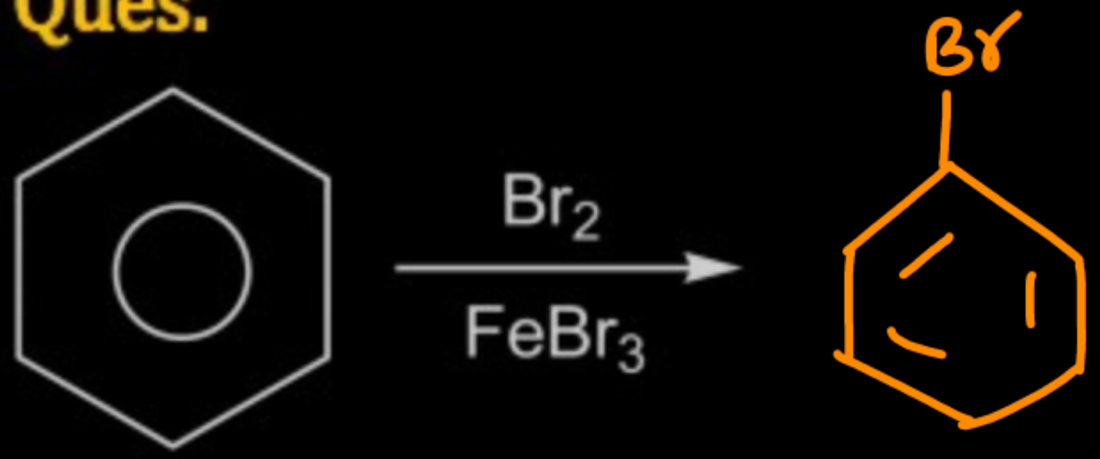
Now a days

Ques.



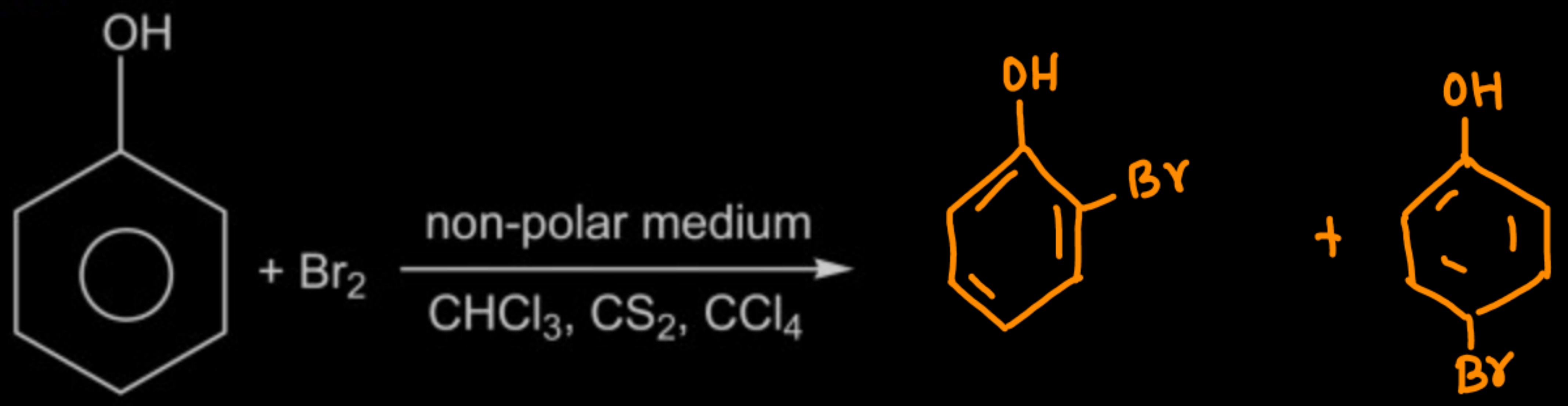
(2) Halogenation:

Ques.

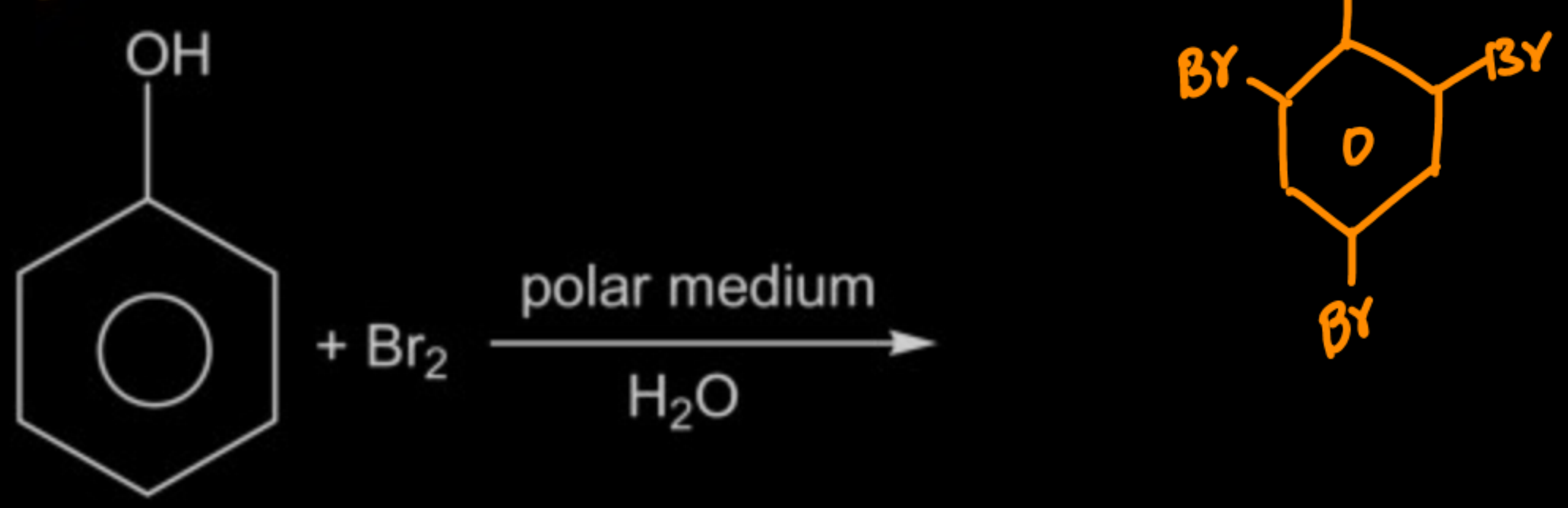


Since Phenol is activating in nature, so lewis acid is not req.

Ques.

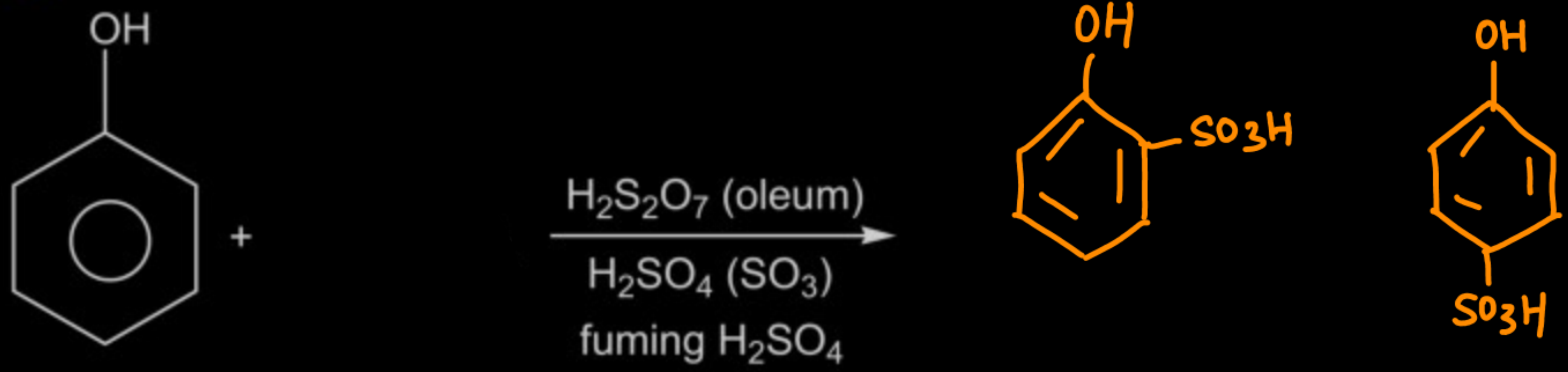


Ques.



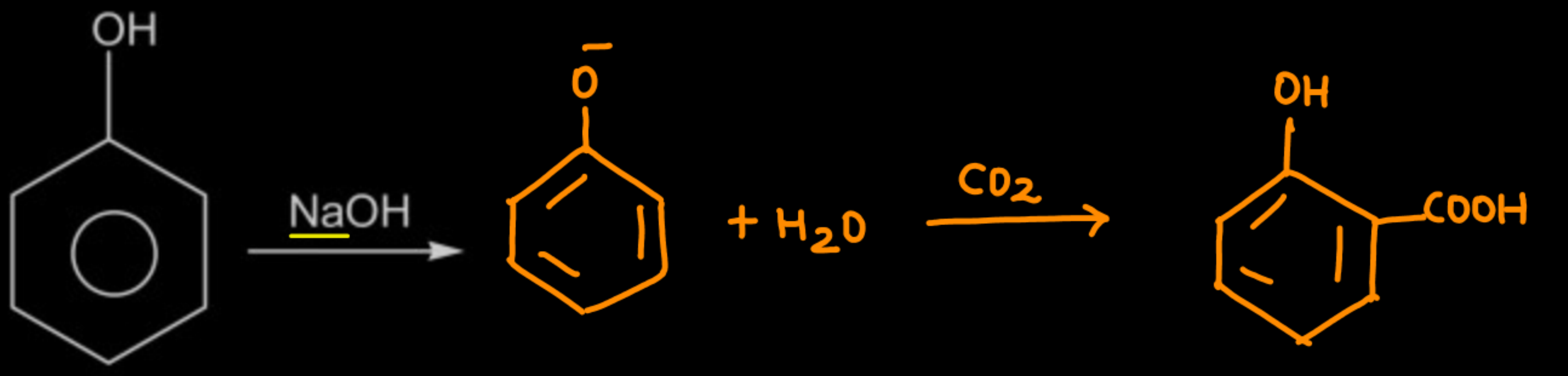
(3) Sulphonation:

Ques.



(4) Kolbe schmidt reaction:

Ques.

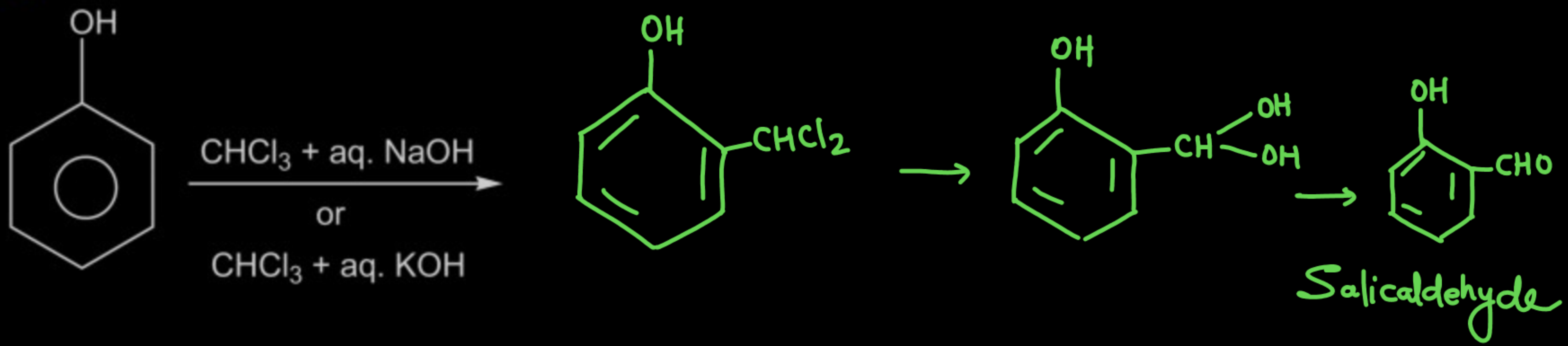


Phenol — Phenoxide ion — Salicyclic acid

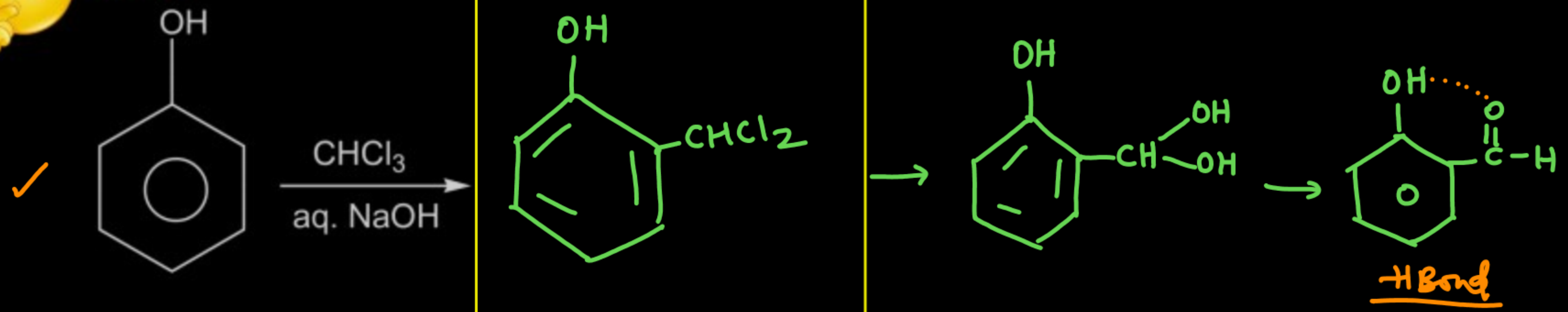
रीमा टीमा Phenol Chloroform Base

(5) Reimer-tieman reaction:

Ques.

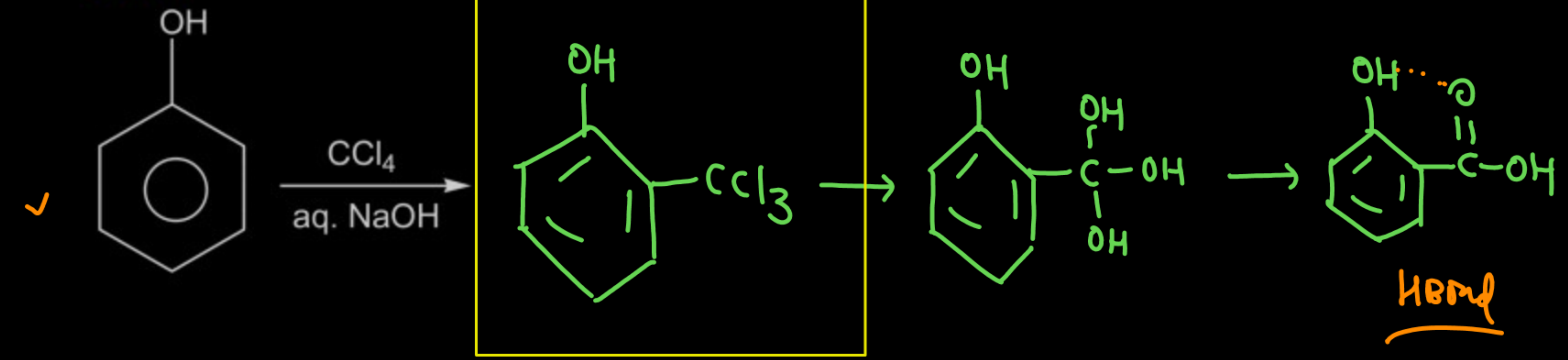


Ques.



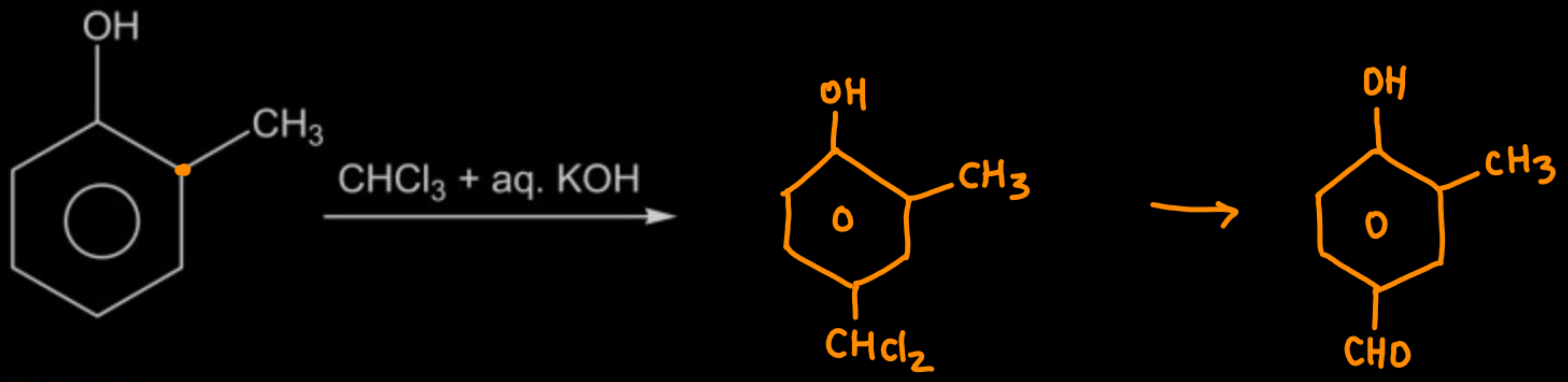
OH
CHCl3
aq. NaOH
OH
CHCl2
OH
CH
OH
OH
OH
O
C
H
H Bond

Ques.

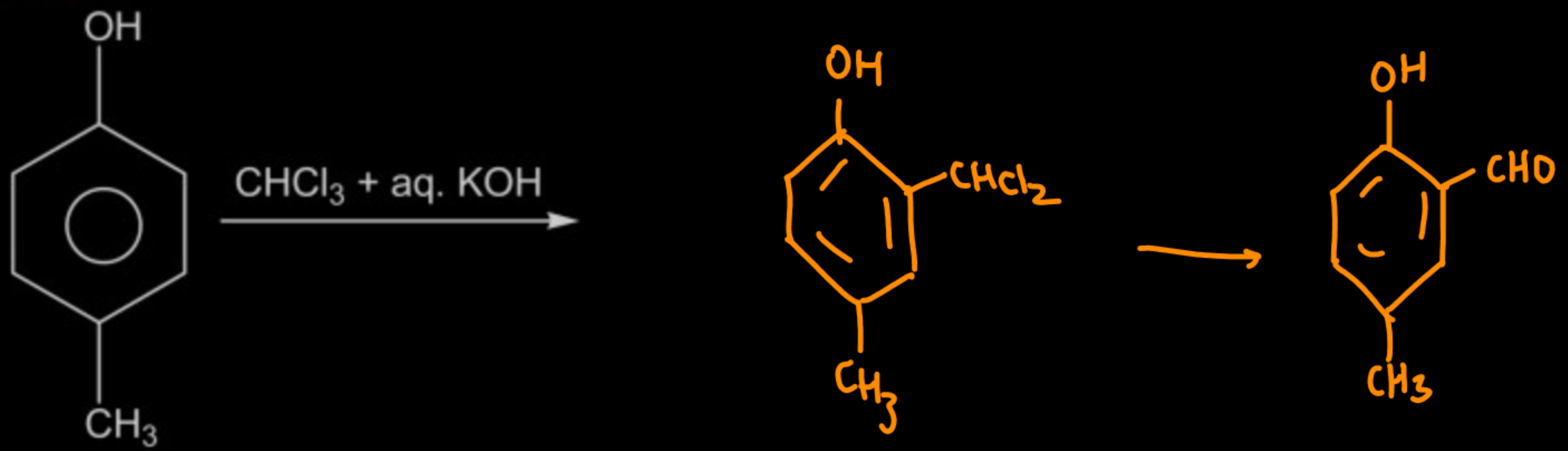


OH
CCl4
aq. NaOH
OH
CCl3
OH
OH
C
OH
OH
OH
O
C
OH
HBond

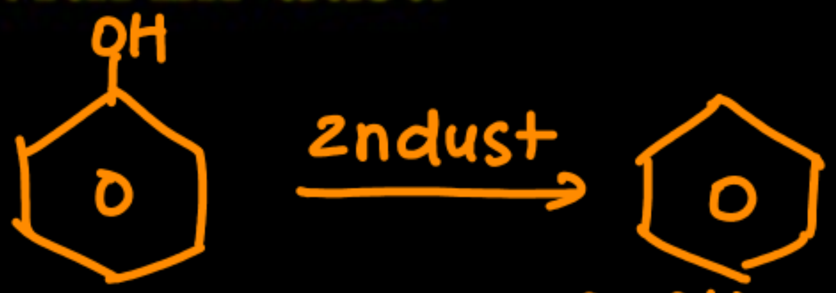
Ques.


OH
CH3
CHCl3 + aq. KOH
OH
CH3
CHCl2
OH
CH3
CHO

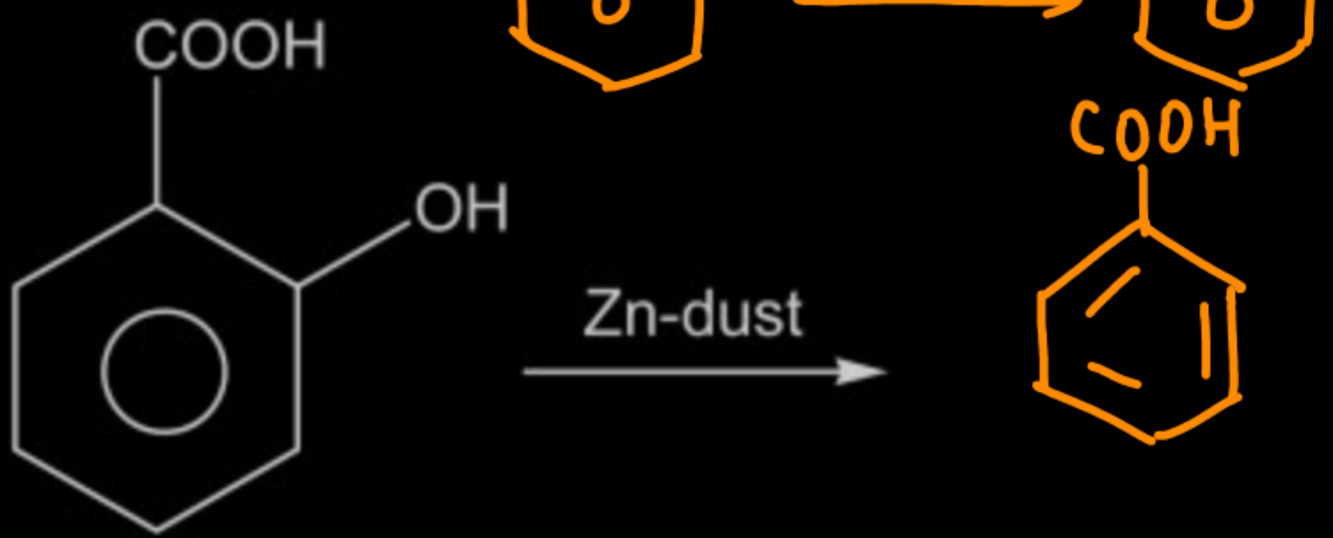
Ques.


OH
CH3
CHCl3 + aq. KOH
OH
CHCl2
CH3
OH
CHO
CH3

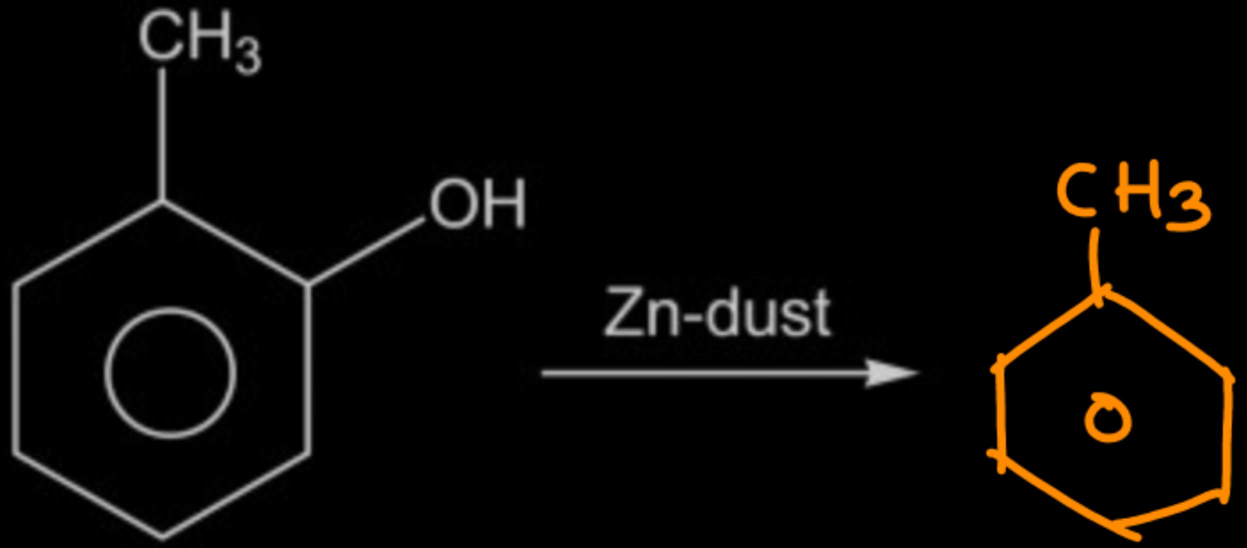
(6) Reaction with Zn-dust:



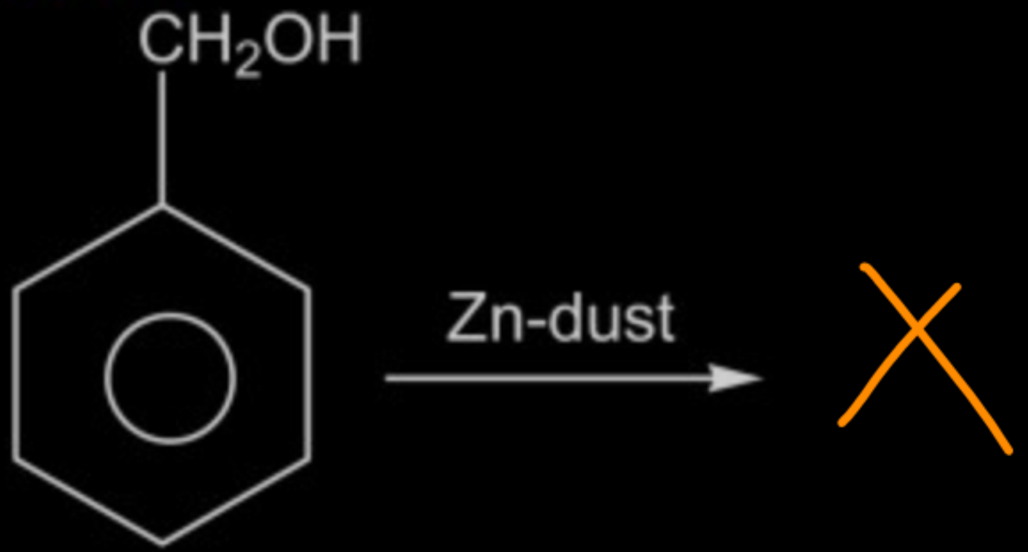
Ques.



Ques.



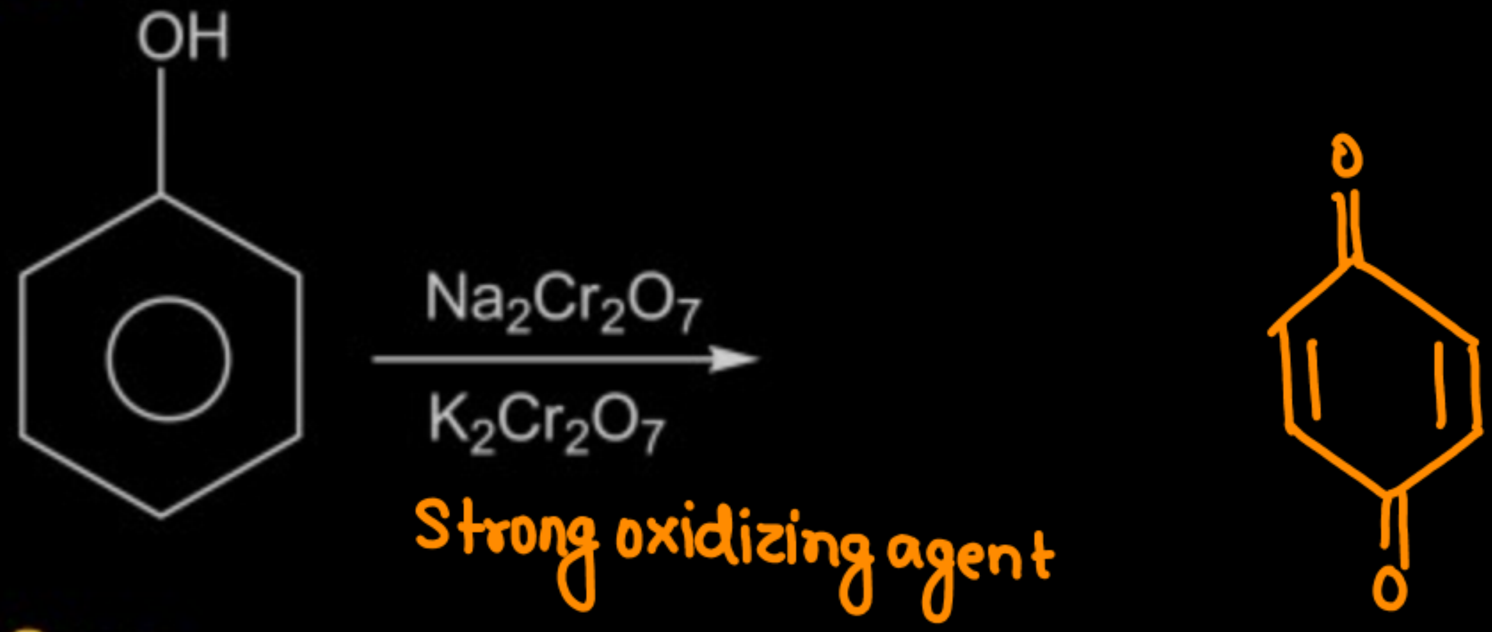
Ques.



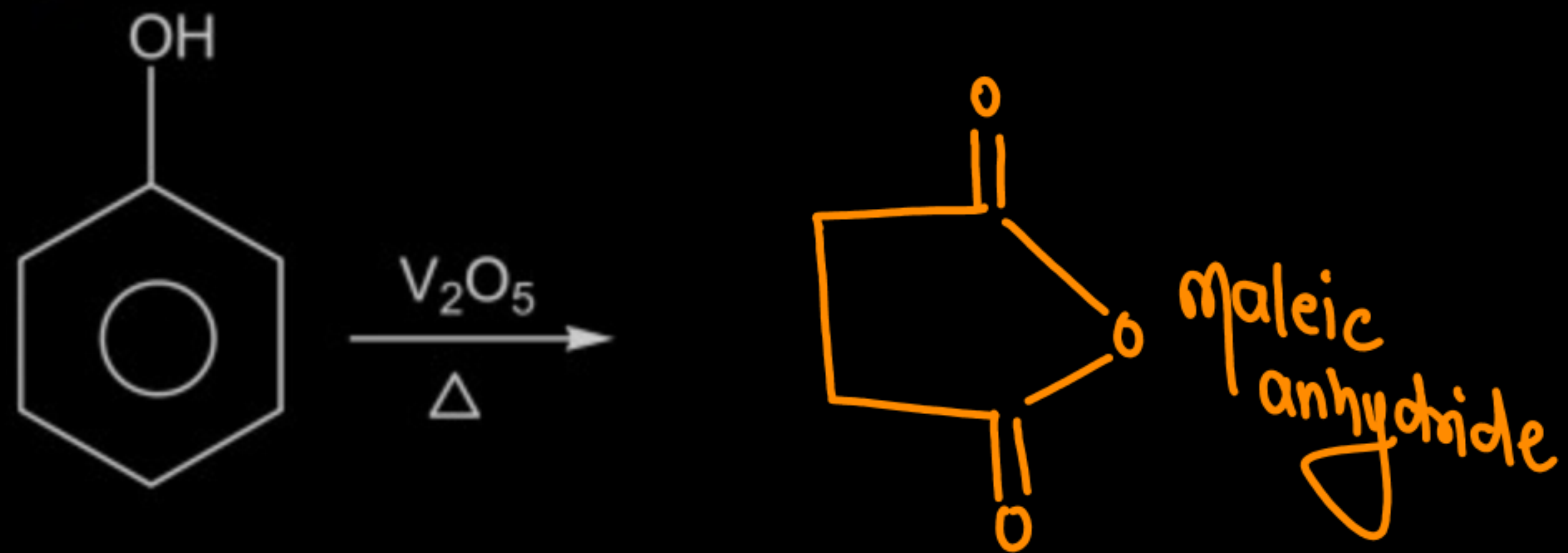


(7) Oxidation of phenol:

Ques.



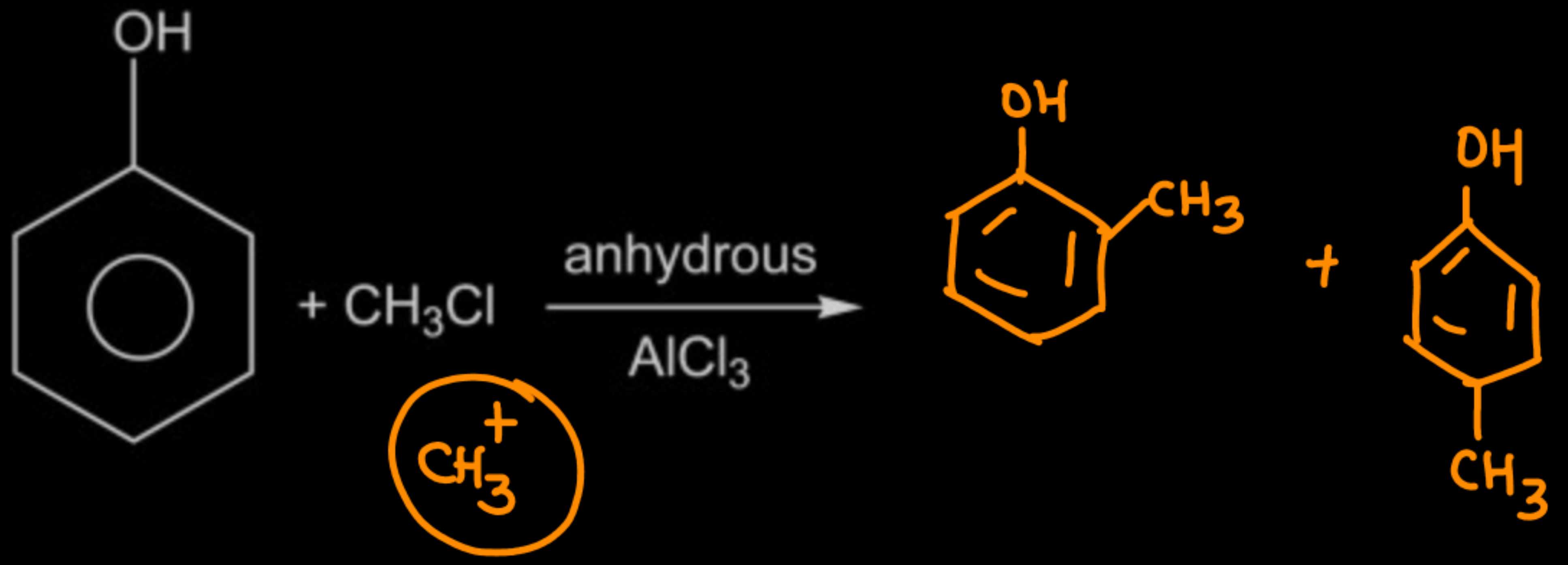
Ques.



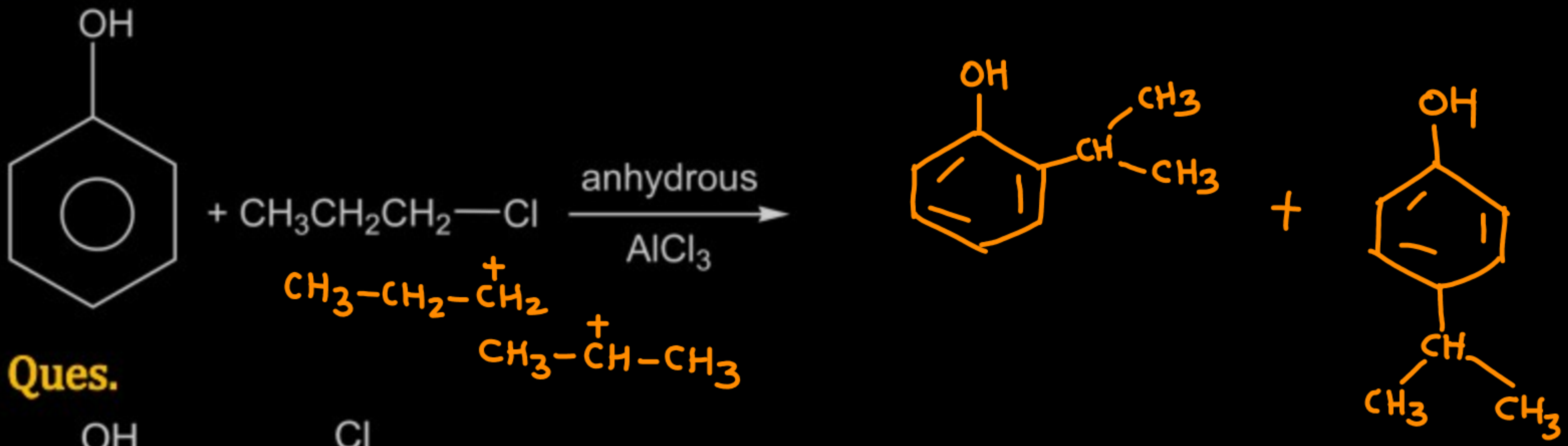
(8) Friedel craft reaction:

⟹ Friedel craft alkylation

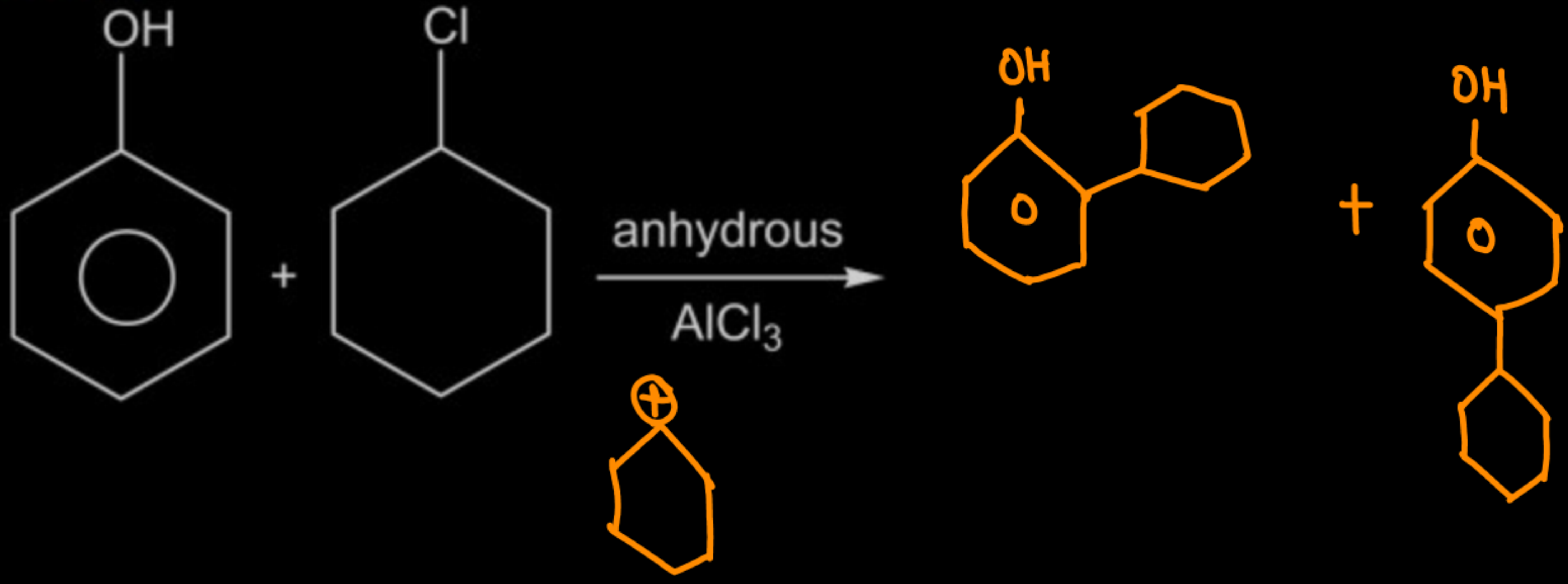
Ques.



Ques.

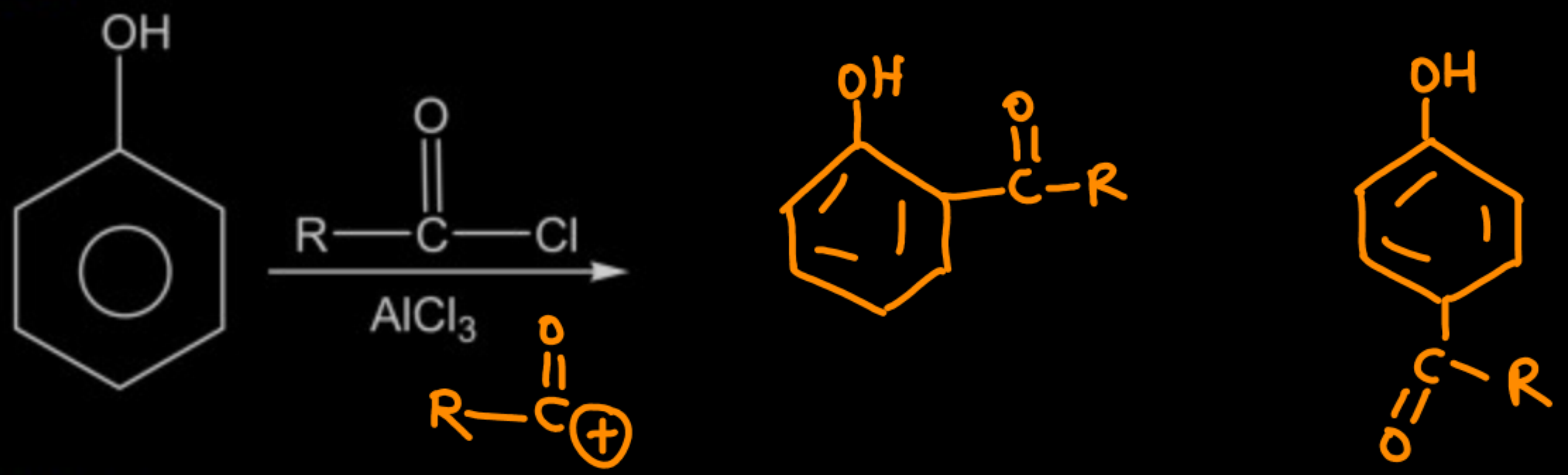

OH
+ CH3CH2CH2—Cl
anhydrous
AlCl3
CH3–CH2–CH2 +
CH3–CH–CH3 +
OH
CH
CH3
CH3
+
OH
CH
CH3
CH3

Ques.

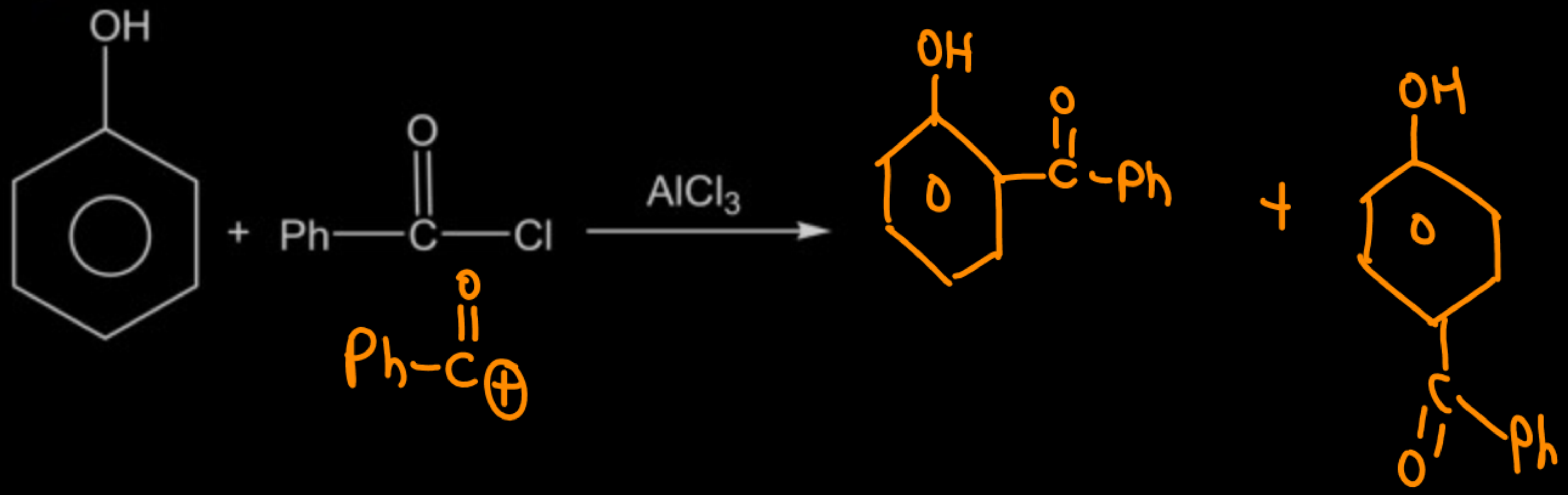

OH
Cl
+
anhydrous
AlCl3
OH
+
OH

⇒ **Friedel craft acylation**

Ques.



Ques.



Ether

Method of Preparation

(i) From Alkene

$$CH_3-CH=CH_2 \xrightarrow[R-O^-]{R-O-H/H^+} CH_3-\overset{\oplus}{C}H-CH_3 \rightarrow CH_3-\underset{OR}{CH}-CH_3$$

→ Carbocation Form.

→ Rearrangement occur.

→ nucleophile attack.

$$CH_3-CH(CH_3)-CH=CH_2 \xrightarrow{C_2H_5OH/H^+} CH_3-CH(CH_3)-\overset{\oplus}{C}H-CH_3$$

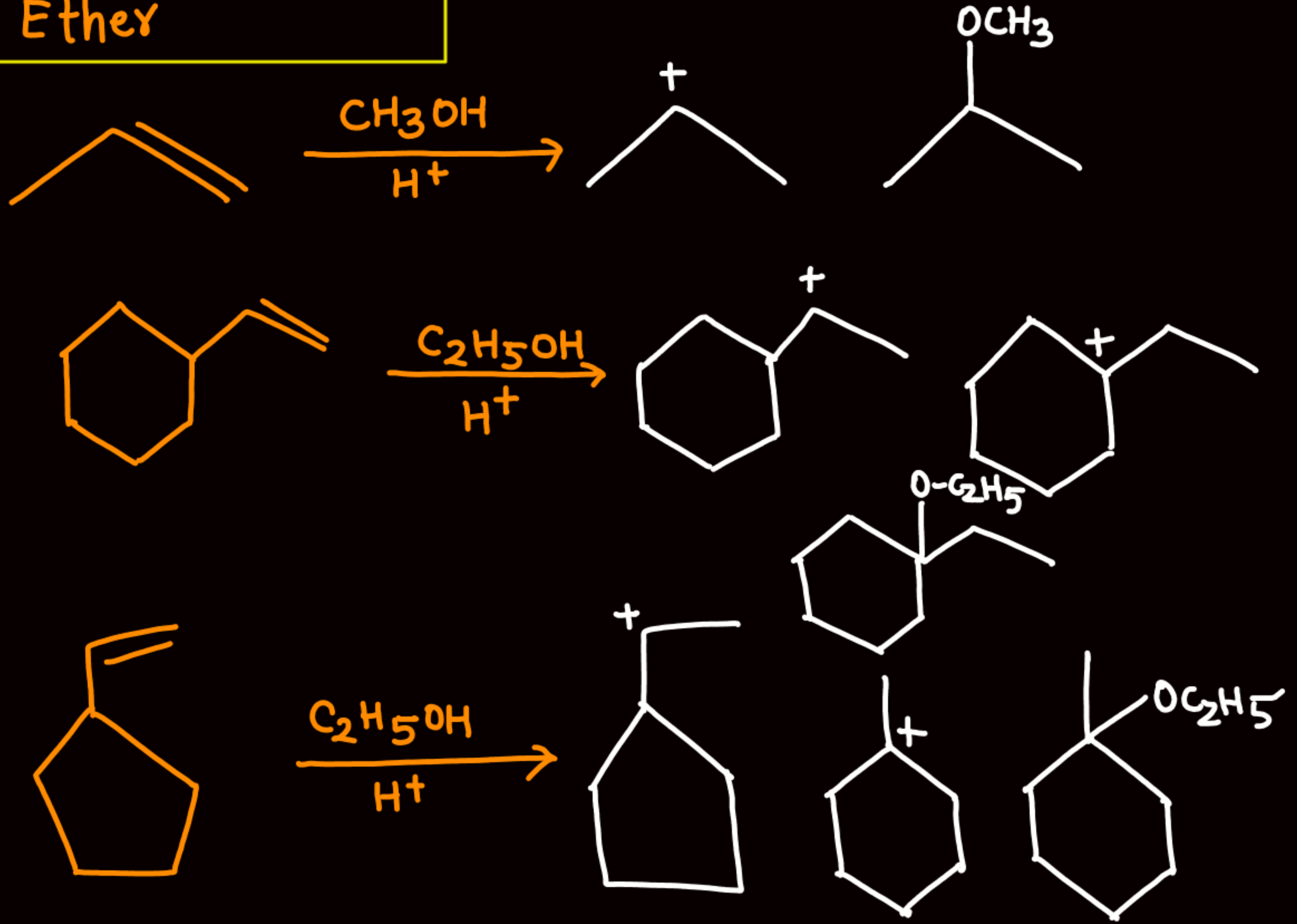
$$CH_3-\overset{\oplus}{C}(CH_3)-CH_2-CH_3$$

$$CH_3-C(CH_3)(O-C_2H_5)-CH_2-CH_3$$

Ether

Method of Preparation

(i) From Alkene



Ether

Method of Preparation

(i) From Alkene

(ii) OMDM

Oxy Mercuration – Demercuration

$CH_3-CH=CH_2 \xrightarrow[NaBH_4/OH^-]{Hg(OAC)_2/H_2O}$ $CH_3-CH(OH)-CH_2-H$

H_2O → OH add

$NaBH_4$ → H add

- Markonicoff Rule
- Anti addition

$CH_3-CH=CH_2 \xrightarrow[NaBH_4/OH^-]{Hg(OAc)_2/CH_3OH}$ $CH_3-CH(OCH_3)-CH_2-H$

CH_3OH → CH_3O^- add

$NaBH_4$ → H add

$CH_3-CH(CH_3)-CH=CH_2 \xrightarrow[NaBD_4/OH^-]{Hg(OAc)_2/C_2H_5OH}$ $CH_3-CH(CH_3)-CH(OC_2H_5)-CH_2-D$

Ether

Method of Preparation

(i) From Alkene

(ii) OMDM

(iii) From Alkyl Halide

(SN^2) (williamson ethyl Synthesis)

(1° alkyl Halide + alkoxide)

↳ ether

$CH_3-CH_2-Cl + CH_3-O^- \rightarrow CH_3-CH_2-O-CH_3$

$CH_3-CH_2-Cl + CH_3-CH(CH_3)-O^- \rightarrow CH_3-CH_2-O-CH(CH_3)-CH_3$

$CH_3-CH_2-Cl + CH_3-C(CH_3)_2-O^- \rightarrow CH_3-CH_2-O-C(CH_3)_2-CH_3$

1° alkyl Halide $\xrightarrow{\text{alkoxide}}$ ether (SN^2)

2° alkyl Halide & 3° alkyl Halide $\xrightarrow{\text{alkoxide}}$ alkene (elimination)

$CH_3-CH(CH_3)-Cl \xrightarrow{CH_3-O^-} CH_3-CH=CH_2$

$CH_3-C(CH_3)_2-Cl \xrightarrow{C_2H_5-O^-} CH_2=C(CH_3)-CH_3$

Method of Preparation

(i) From Alkene

(ii) OMDM

(iii) From Alkyl Halide
(S_N2)(williamson ethyl Synthesis)
(1° alkyl Halide + alkoxide)
↳ ether

(iv) From Alcohol
↳ dehydration
↳ H_2O Removal

Ether

(i)

$CH_3-CH_2-CH_2-OH$ (β at the first CH_2, α at the second CH_2; alcohol)

$\xrightarrow[100°C]{Conc\ H_2SO_4} CH_3-CH_2-CH_2-HSO_4$

$\xrightarrow[140°C]{Conc\ H_2SO_4}$ ether $CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$

$\xrightarrow[170°C]{Conc\ H_2SO_4} CH_3-CH=CH_2$ (elimination)

(ii) Using CH_2N_2 (diazomethane)

$$CH_3-CH_2-OH + CH_2N_2 \longrightarrow CH_3-CH_2-O-CH_3$$

$$CH_3-OH + CH_2N_2 \longrightarrow CH_3-O-CH_3$$

Ether

Method of Preparation

(i) From Alkene

(ii) OMDM

(iii) From Alkyl Halide

(S_N2) (williamson ethyl Synthesis)

(1° alkyl Halide + alkoxide)

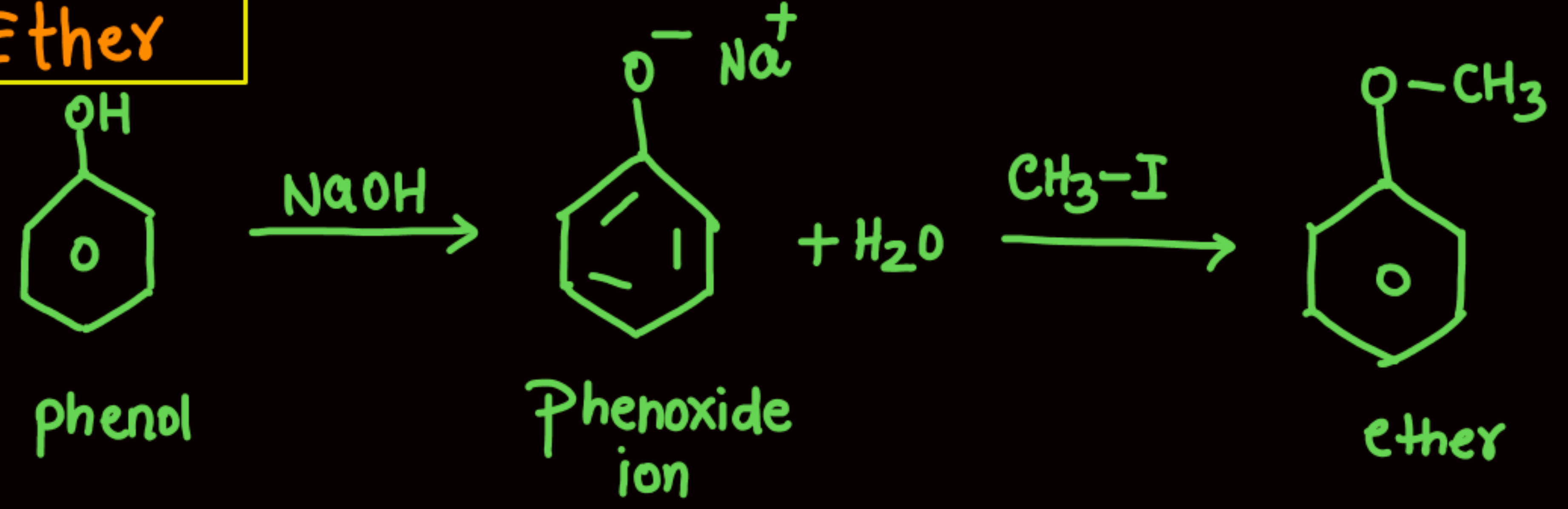
↳ ether

(iv) From Alcohol

↳ dehydration

↳ H_2O Removal

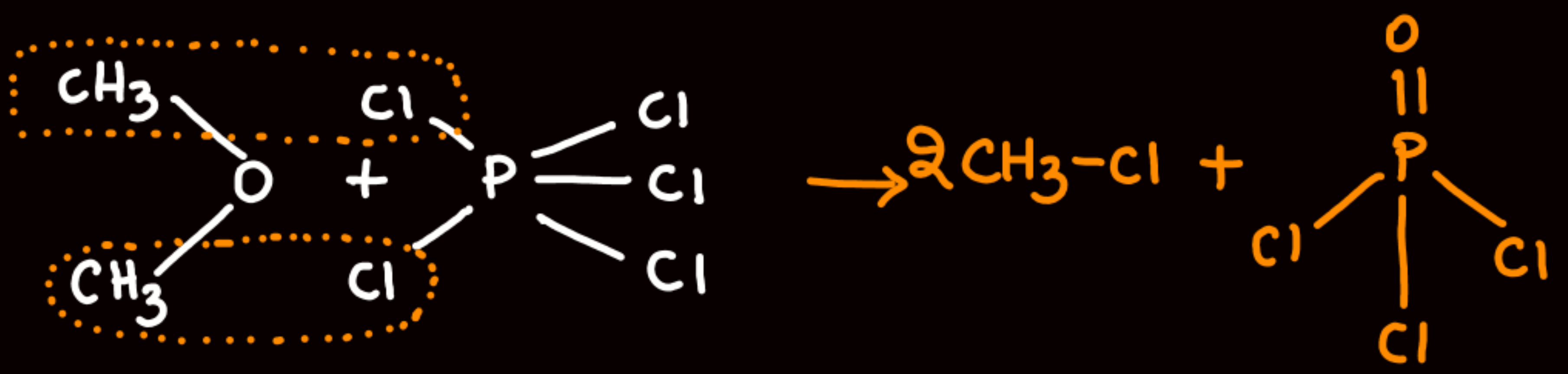
(v) From phenol

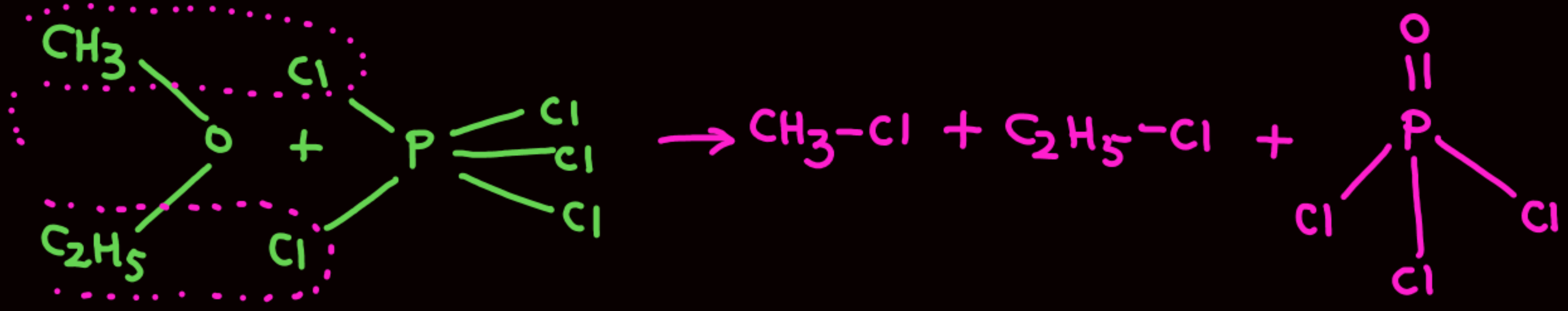


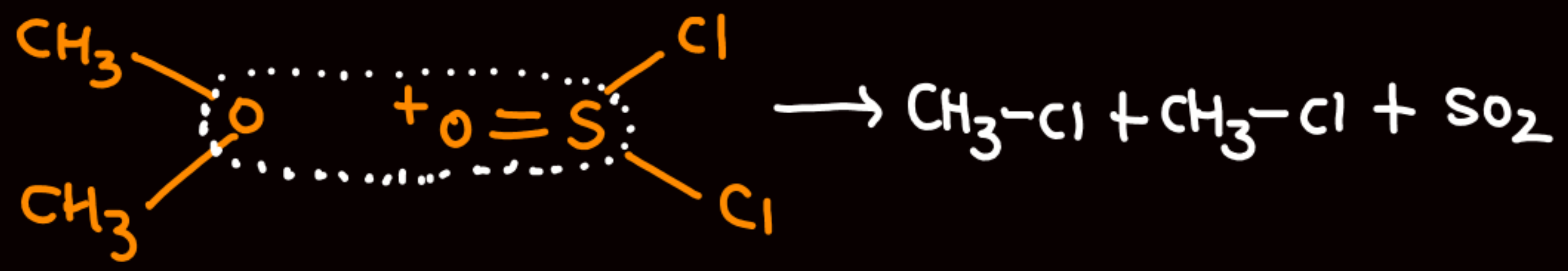
Chemical Reaction of Ether

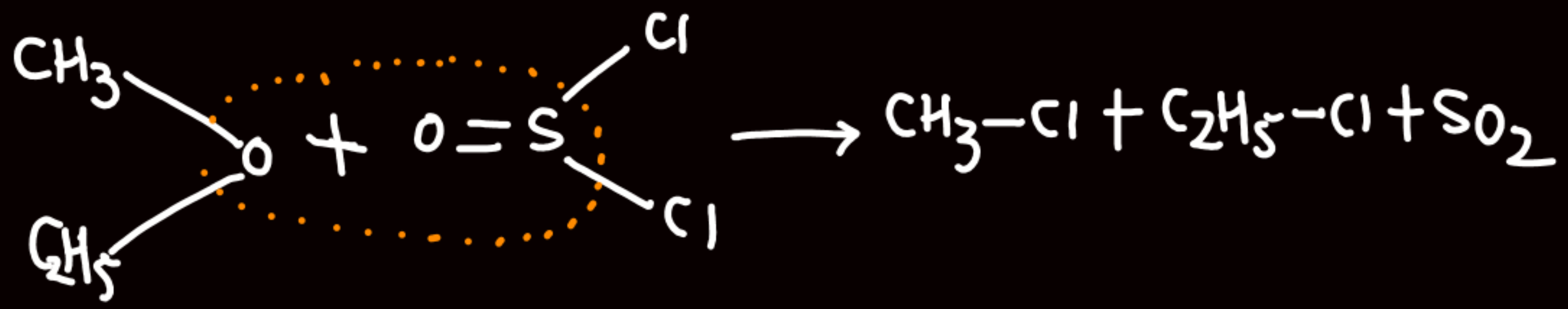
① Reaction with PCl_5

② Reaction with $SOCl_2$









Chemical Reaction of Ether

① Reaction with PCl_5

② Reaction with $SOCl_2$

③ Reaction with Red P & HI

$$CH_3-O-CH_3 \xrightarrow[HI]{Red\,P} CH_4 + CH_4$$

$$CH_3-O-C_2H_5 \xrightarrow{\text{"}} CH_4 + C_2H_6$$





Chemical Reaction of Ether

1. Reaction with PCl_5
2. Reaction with $SOCl_2$
3. Reaction with Red P & HI
4. Halogenation

$$CH_3-CH_2-\ddot{O}-CH_2-CH_3 \xrightarrow{1\,Cl_2} CH_3-CH_2-O-CH(Cl)-CH_3$$

$$\xrightarrow{2\,Cl_2} CH_3-CH(Cl)-O-CH(Cl)-CH_3$$

$$\xrightarrow{10\,Cl_2} CCl_3-CCl_2-O-CCl_2-CCl_3$$

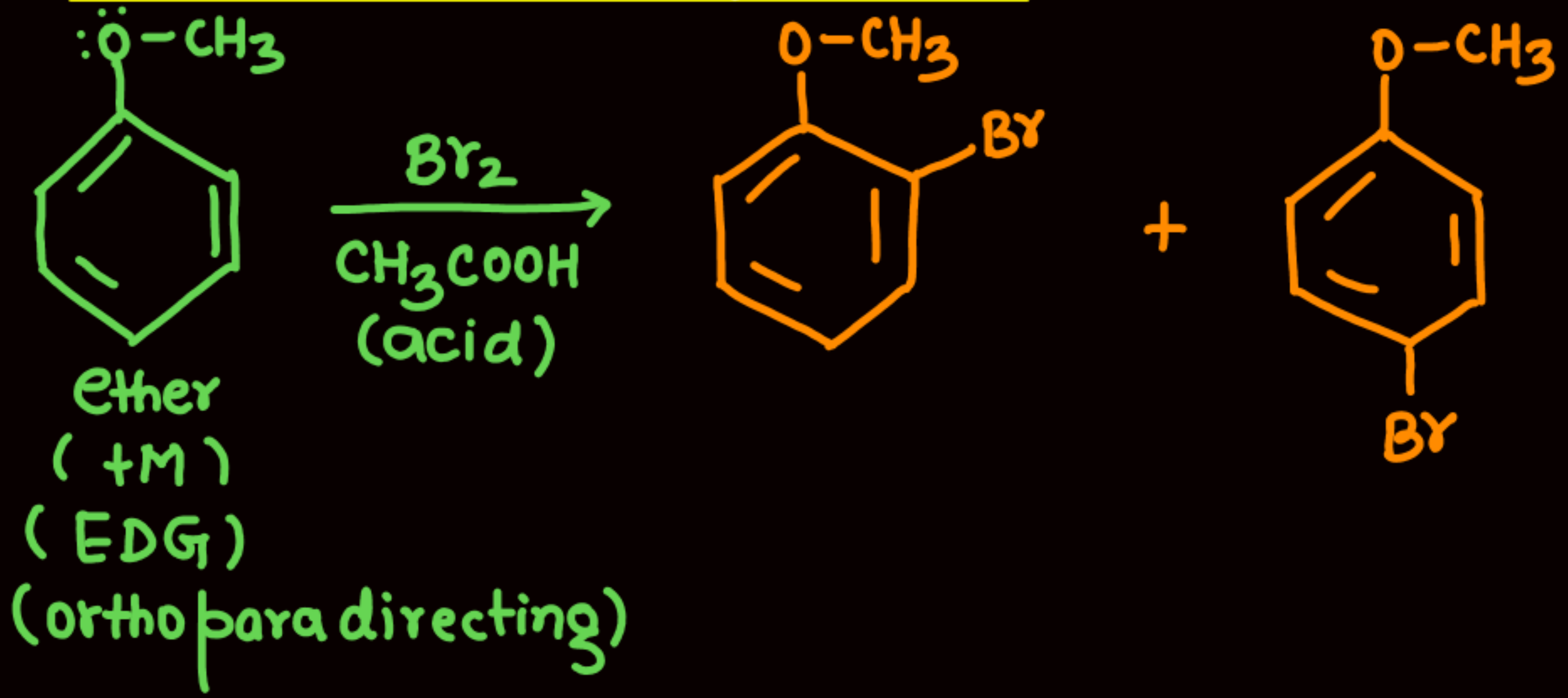
$$CH_3-CH_2-O-CH_2-Ph \xrightarrow{1\,Cl_2} CH_3-CH_2-O-CH(Cl)-Ph$$

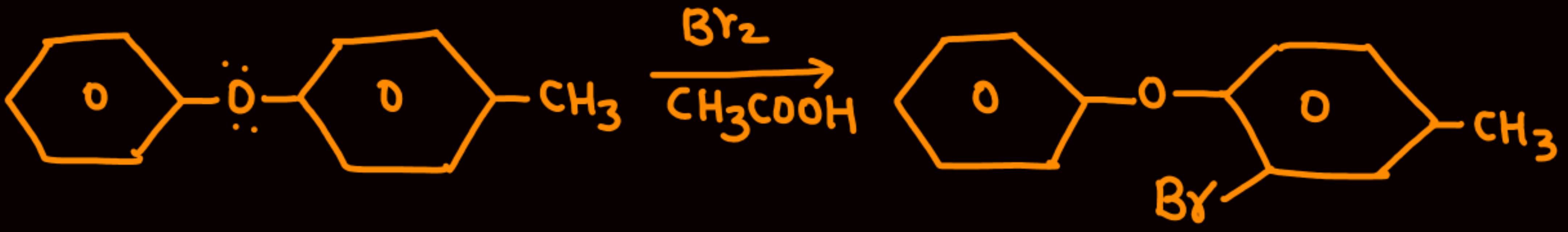
$$\xrightarrow{2\,Cl_2} CH_3-CH(Cl)-O-CH(Cl)-Ph$$

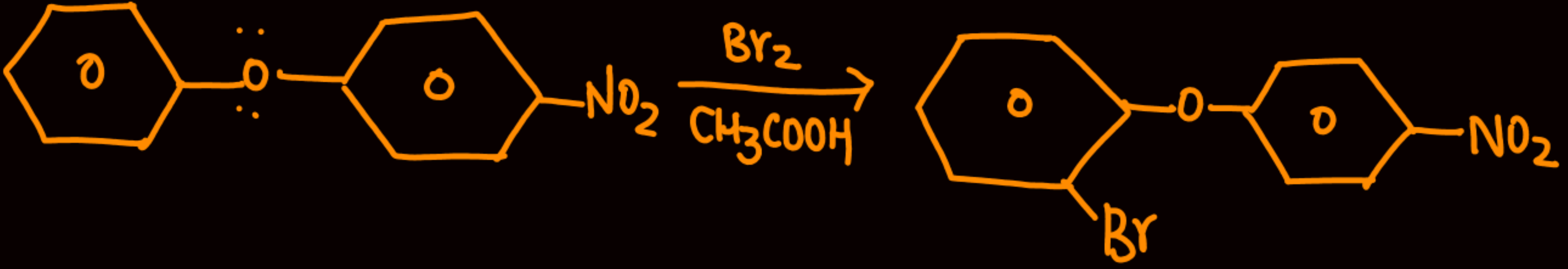
$$\xrightarrow{10\,Cl_2} CCl_3-CCl_2-O-CCl_2-Ph$$

Chemical Reaction of Ether

1. Reaction with PCl_5
2. Reaction with $SOCl_2$
3. Reaction with Red P & HI
4. Halogenation



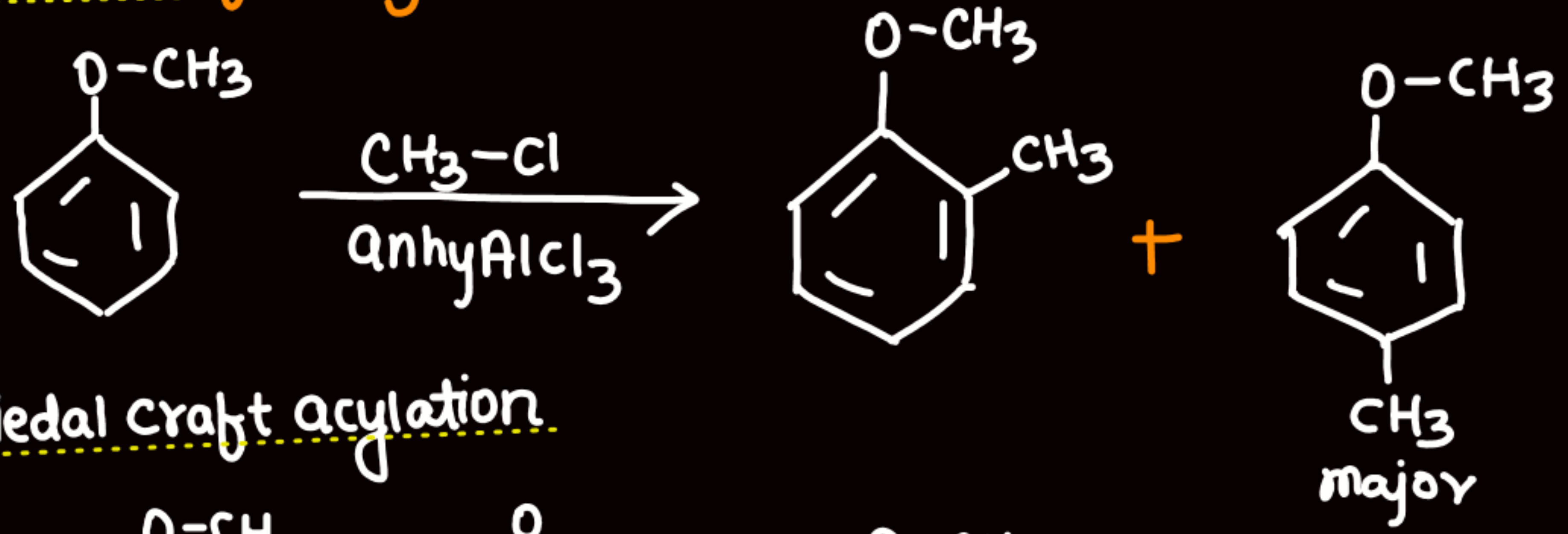




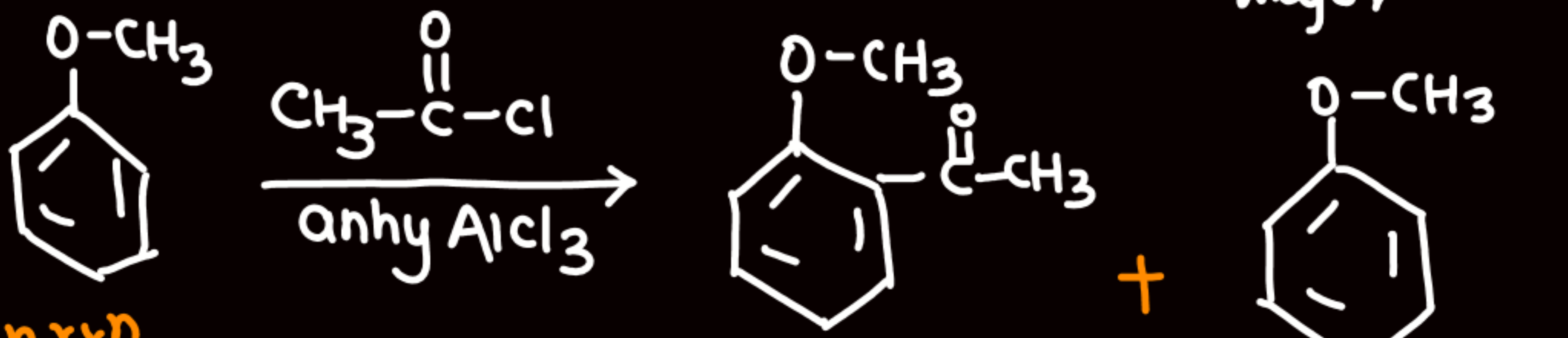
Chemical Reaction of Ether

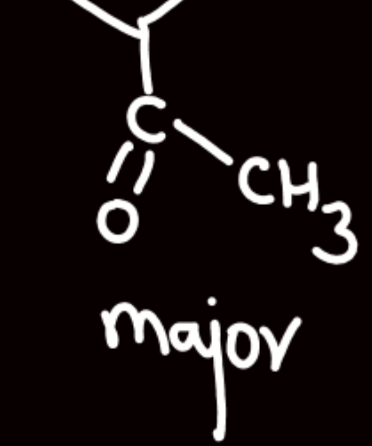
1. Reaction with PCl_5
2. Reaction with $SOCl_2$
3. Reaction with Red P & HI
4. Halogenation
5. Friedal craft Rxn
6. nitration
7. Reaction with HI

Friedal Craft Alkylation

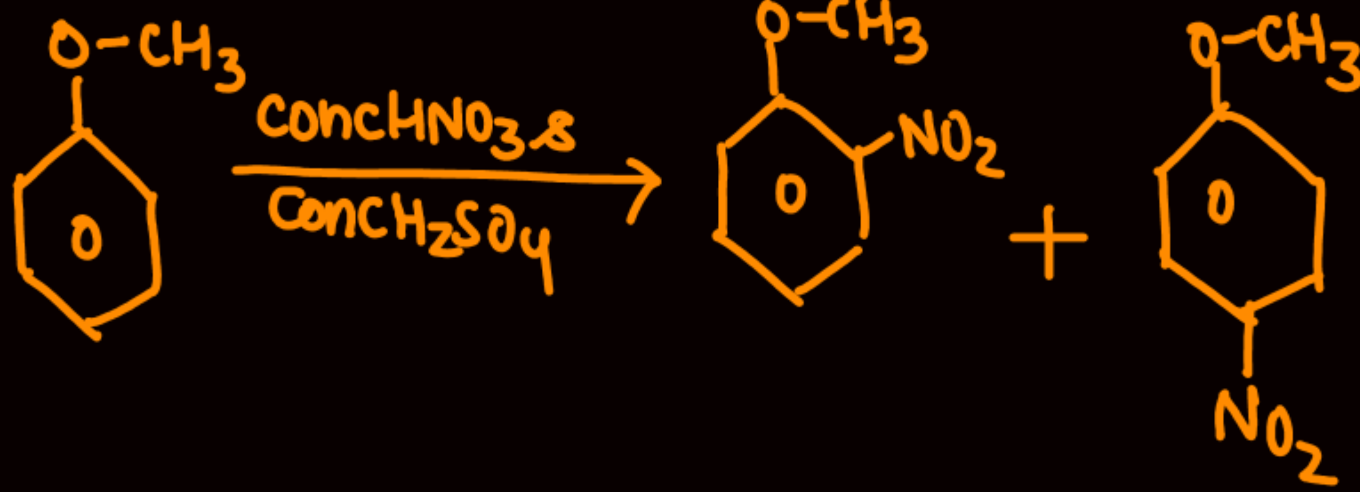


Friedal craft acylation





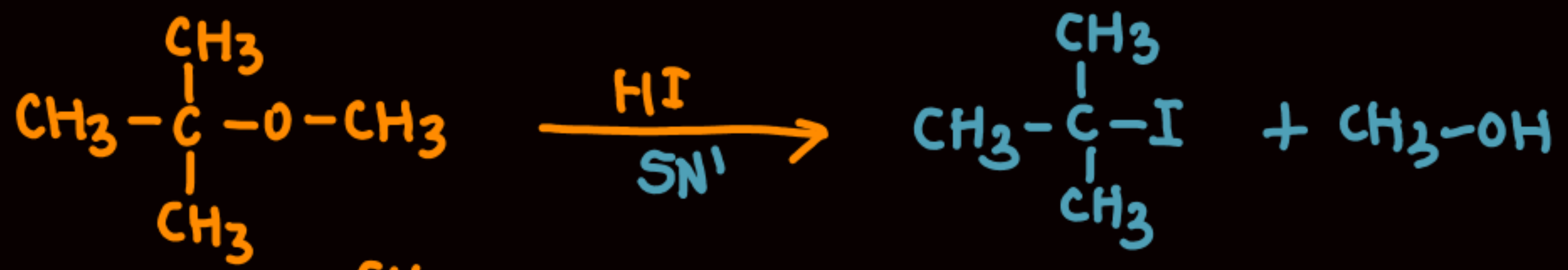
nitration rxn

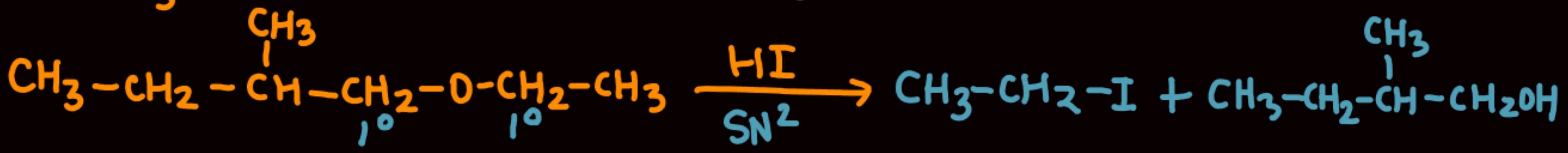


Chemical Reaction of Ether

1. Reaction with PCl_5
2. Reaction with $SOCl_2$
3. Reaction with Red P & HI
4. Halogenation
5. Friedal craft Rxn
6. nitration
7. Reaction with HI

$$CH_3-O-CH_2-CH_2-CH_3 \xrightarrow[SN^2]{HI} CH_3I + CH_3-CH_2-CH_2-OH$$









Preparation of Both Aldehyde & Ketone

① Alkene $\xrightarrow{\text{ozonolysis}}$

Alkyne $\xrightarrow{\text{Ozonolysis}}$

① Reductive Ozonolysis $\xrightarrow[Zn,\ H_2O]{O_3}$

② Oxidative Ozonolysis $\xrightarrow[H_2O]{O_3}$

② Hydration of alkyne $\xrightarrow[H_2SO_4]{HgSO_4}$ Kucherov's Reaction (H & OH is added by MK Rule)

③ OMDM (Oxymercuration DeMercuration) $\xrightarrow[NaBH_4/OH^-]{Hg(OAc)_2/H_2O}$ (H & OH is added by MK Rule)

④ HBO (Hydroboration oxidation) $\xrightarrow[H_2O_2/OH^-]{B_2H_6}$ H & OH is added by AMK Rule.

⑤ Oxidation of alcohol $\xrightarrow[\text{Oxidising Agent}]{\text{Strong}}$ $H^+/KMnO_4$ or $H^+/K_2Cr_2O_7$ or $(CrO_3 + H_2SO_4)$ Jone's Reagent

⑥ DeHydrogenation of Alcohol $\xrightarrow[300°C]{Cu/Ag}$

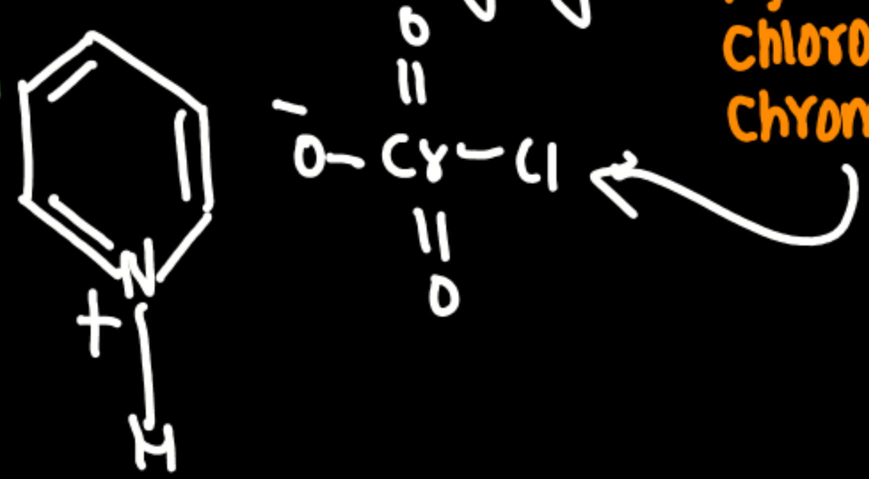
⑦ oxidation of diols $\xrightarrow[\text{Oxidising Agent}]{\text{Mild}}$ PCC or PDC

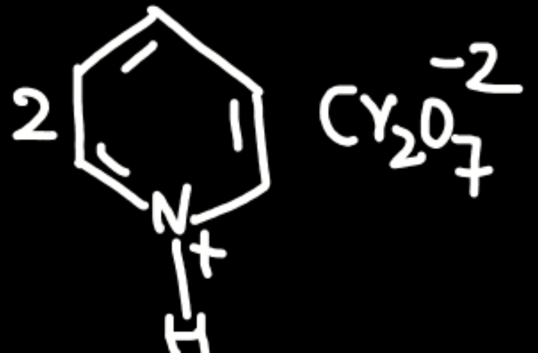
PCC: pyridinium chloro chromate

PDC: pyridinium dichromate

⑧ Thermal decomposition of Carboxylic acid

⑨ Hydrolysis of Halide





(10) Hydrolysis of Carbonyl Derivative

(11) Heating of β keto acid

(12) From Grignard

(1) From Hydrocarbon: -

(i) Ozonolysis of Alkenes:

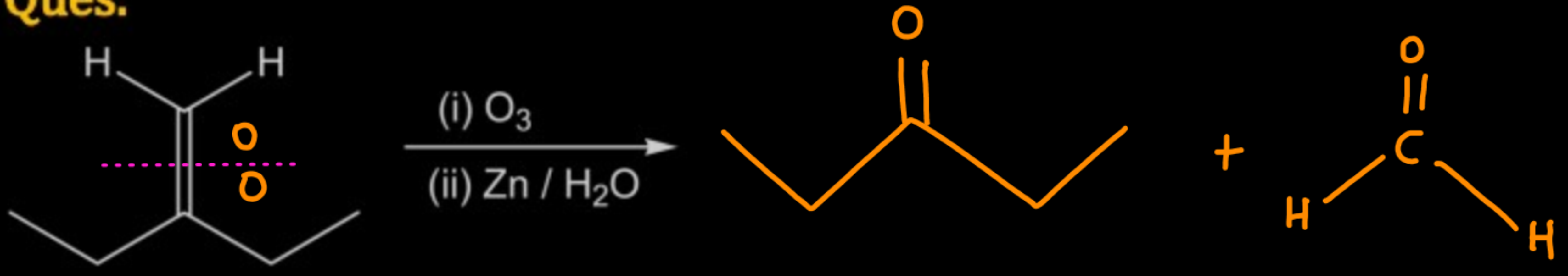
Ques.

$$R - CH_2 = CH_2 + O_3 \xrightarrow{Zn / H_2O} R-\overset{\overset{O}{\|}}{C}-H + H-\overset{\overset{O}{\|}}{C}-H$$

Ques.

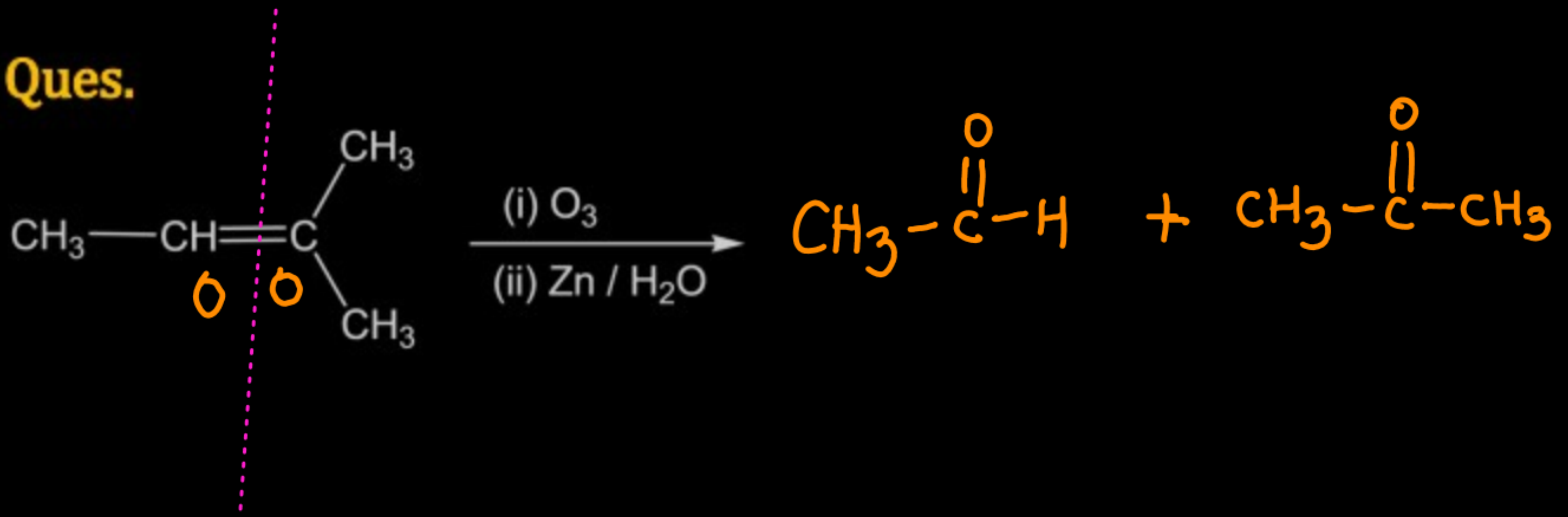
$$R - \underset{\underset{R}{|}}{C} = CH_2 + O_3 \xrightarrow{Zn / H_2O} R-\overset{\overset{O}{\|}}{C}-R + H-\overset{\overset{O}{\|}}{C}-H$$

Ques.



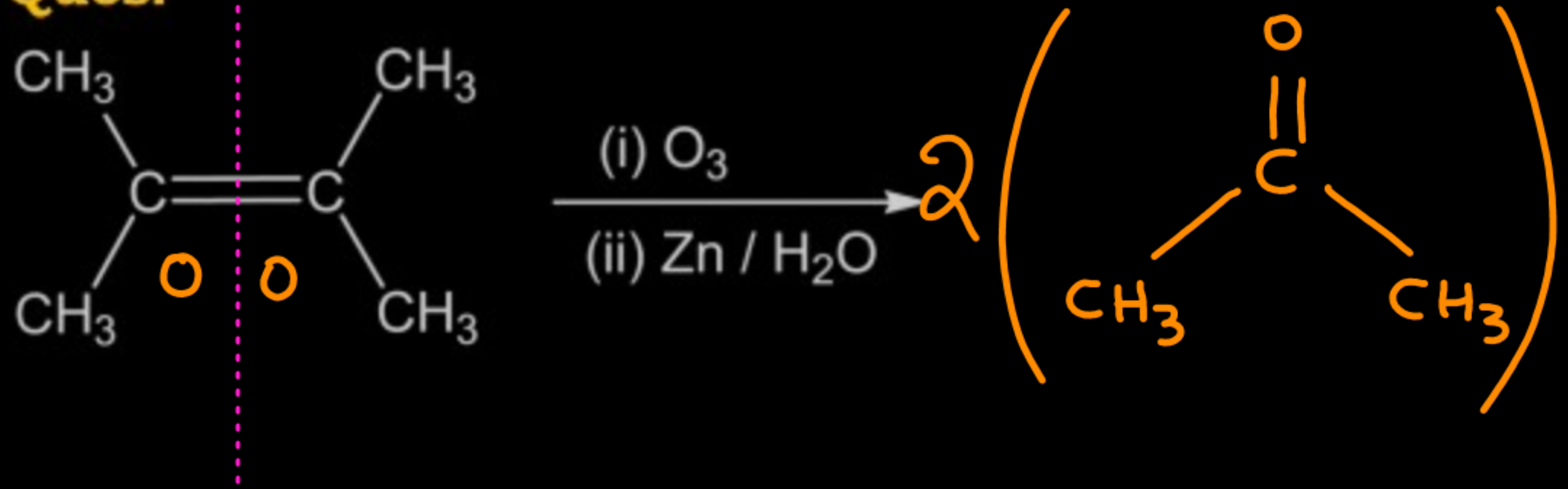
H
H
O
O
(i) O_3
(ii) Zn / H_2O
O
O
C
H
H
+

Ques.



CH_3—CH═C
CH_3
CH_3
O
O
(i) O_3
(ii) Zn / H_2O
$CH_3-\overset{O}{\overset{\|}{C}}-H$ + $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

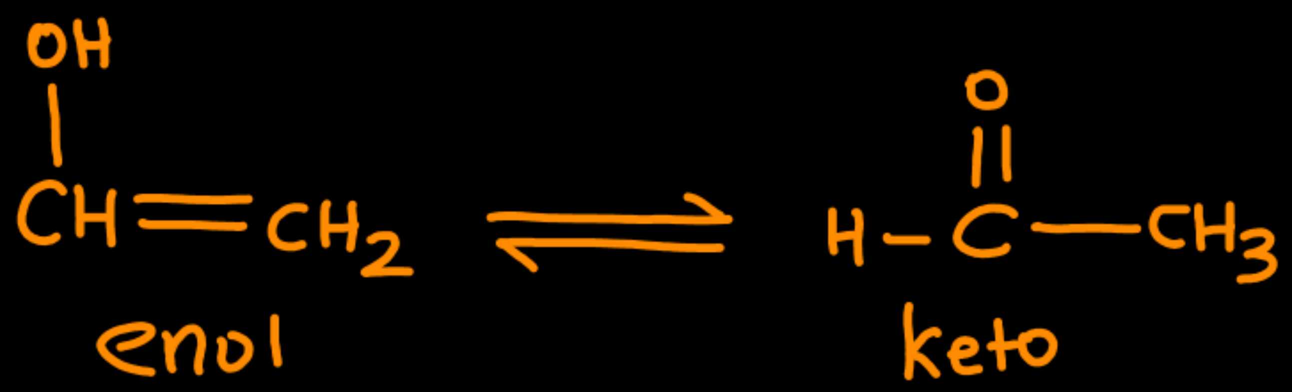
Ques.



(ii) Hydration of Alkenes:

Ques.

$$CH \equiv CH + H_2O \xrightarrow[1\%\ HgSO_4]{dil\ H_2SO_4}$$



Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[1\%\ HgSO_4]{dil\ H_2SO_4} \underset{enol}{CH_3-CH=\overset{OH}{\overset{|}{C}}-CH_3} \rightleftharpoons \underset{keto}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}$$

Ques.

$$CH_3-CH_2-C\equiv CH \xrightarrow[1\%\ HgSO_4]{dil\ H_2SO_4} \underset{enol}{CH_3-CH_2-\overset{OH}{\overset{|}{C}}=CH_2} \rightleftharpoons \underset{keto}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3}$$

Ques.

$$R-C\equiv CH \xrightarrow[\text{(ii) } H_2O_2\,/\,OH^-]{\text{(i) } B_2H_6} \underset{\text{(enol)}}{R-CH=CH-OH} \rightleftharpoons \underset{\text{(Keto)}}{R-CH_2-\overset{O}{\overset{\|}{C}}-H}$$

HBO

Ques.

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2O_2\,/\,OH^-]{B_2H_6} \underset{\text{enol}}{CH_3-CH=\overset{\overset{OH}{|}}{C}-CH_3} \rightleftharpoons \underset{\text{Keto}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

Ques.

$$CH_3-CH_2-C\equiv CH \xrightarrow[NaBH_4]{Hg(OAc)_2\,/\,H_2O} \underset{\text{enol}}{CH_3-CH_2-\overset{\overset{OH}{|}}{C}=CH_2} \rightleftharpoons \underset{\text{keto}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

(Mk Rule)

Oxidation of Alcohol

$CH_3-CH_2-CH_2-OH \xrightarrow{H^+/KMnO_4} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$

1° alcohol

$\xrightarrow{H^+/K_2Cr_2O_7}$,,

$\xrightarrow{CrO_3 + H_2SO_4}$,,

$CH_3-CH_2-CH_2-OH \xrightarrow{PCC} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

$\xrightarrow{PDC}$,,

$CH_3-\underset{CH_3}{\underset{|}{CH}}-OH \xrightarrow{H^+/KMnO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

2° alcohol

$\xrightarrow{H^+/K_2Cr_2O_7}$,,

$\xrightarrow{CrO_3 + H_2SO_4}$,,

> Mild O.A.

1° Alcohol $\xrightarrow[\text{or PDC}]{\text{PCC}}$ aldehyde

2° Alcohol $\xrightarrow[\text{or PDC}]{\text{PCC}}$ ketone

3° Alcohol $\xrightarrow[\text{or PDC}]{\text{PCC}}$ X

> Strong oxidising agent

1° Alcohol $\xrightarrow{H^+/KMnO_4}$, $\xrightarrow{H^+/K_2Cr_2O_7}$, $\xrightarrow{CrO_3 + H_2SO_4}$ Acid

2° Alcohol $\xrightarrow{H^+/KMnO_4}$, $\xrightarrow{H^+/K_2Cr_2O_7}$, $\xrightarrow{CrO_3 + H_2SO_4}$ Ketone

3° alcohol $\longrightarrow$ X

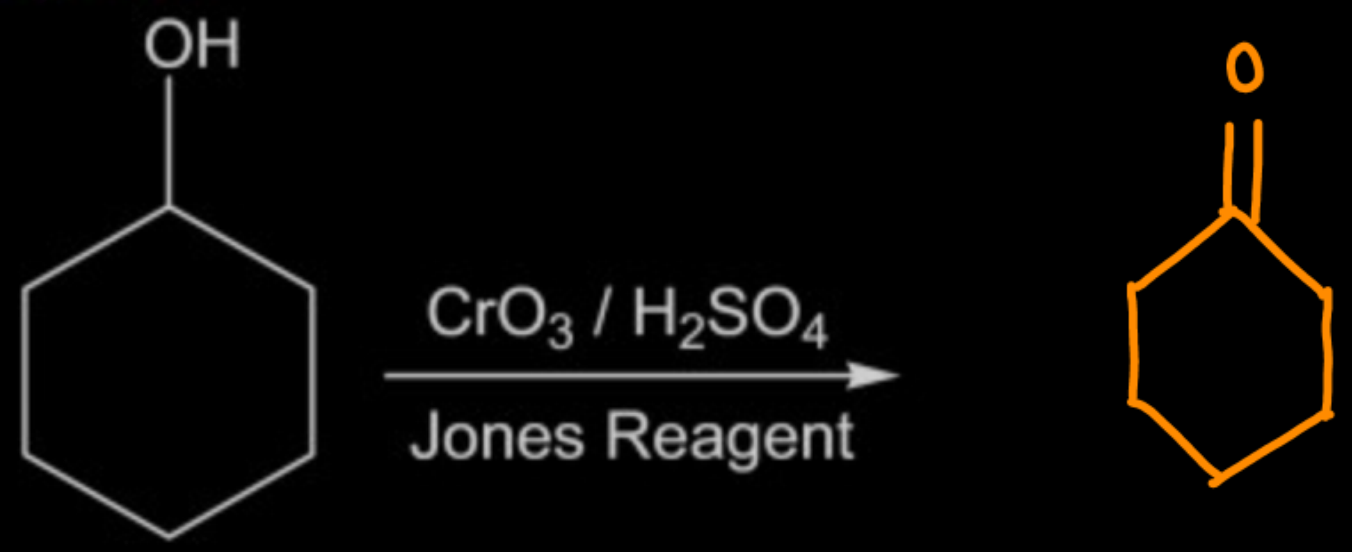
Ques.

$$R - CH_2 - OH \xrightarrow[\text{Mild O.A.}]{\text{PCC}} R-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

Ques.

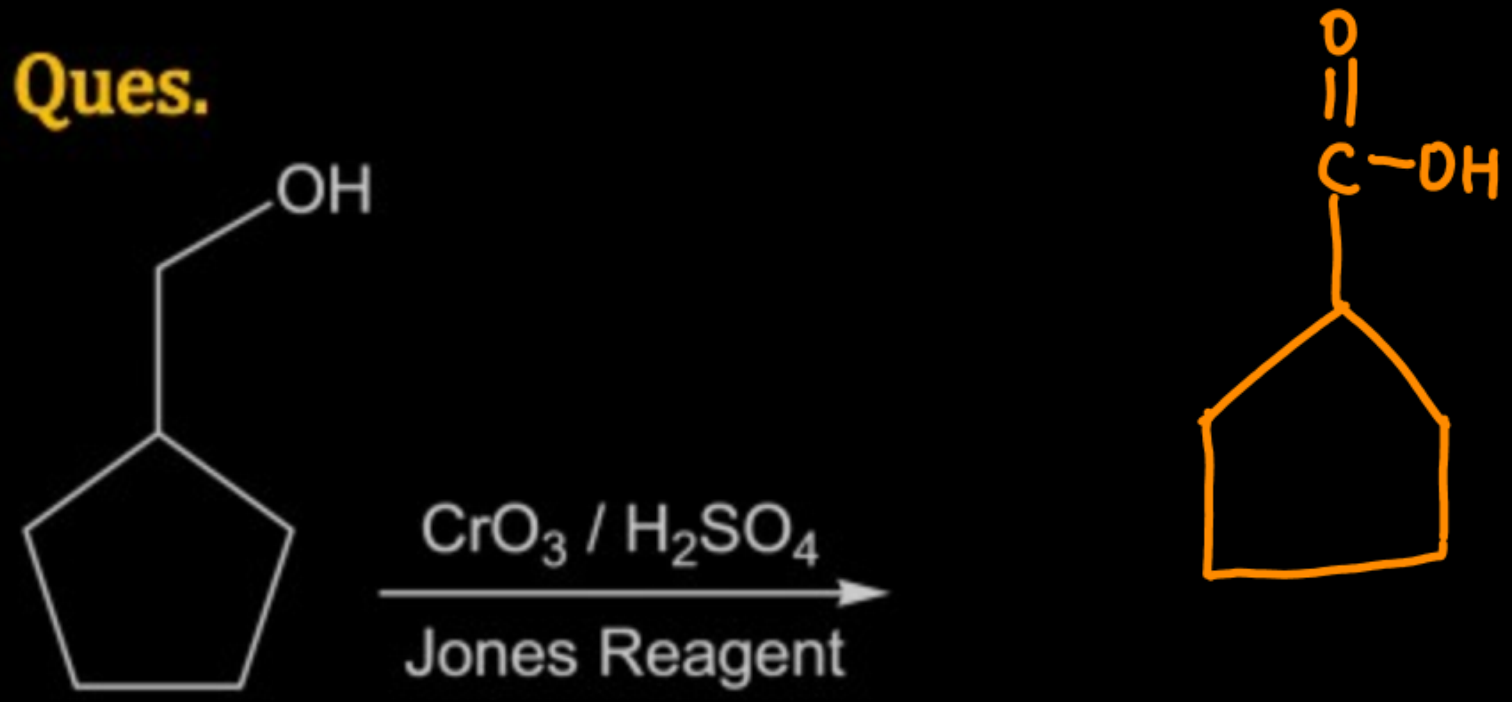
$$R - \overset{\overset{\displaystyle OH}{|}}{C}H - R \xrightarrow[\text{Mild O.A.}]{\text{PCC}} R-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

Ques.



OH
CrO_3 / H_2SO_4
Jones Reagent
O

Ques.



OH
CrO_3 / H_2SO_4
Jones Reagent
O
C
OH

(ii) Dehydrogenation of Alcohol:

Ques.

$$CH_3 - CH_2 - OH \xrightarrow[300^\circ C]{Cu / Ag} CH_3 - \overset{\overset{O}{\parallel}}{C} - H$$

aldehyde

Ques.

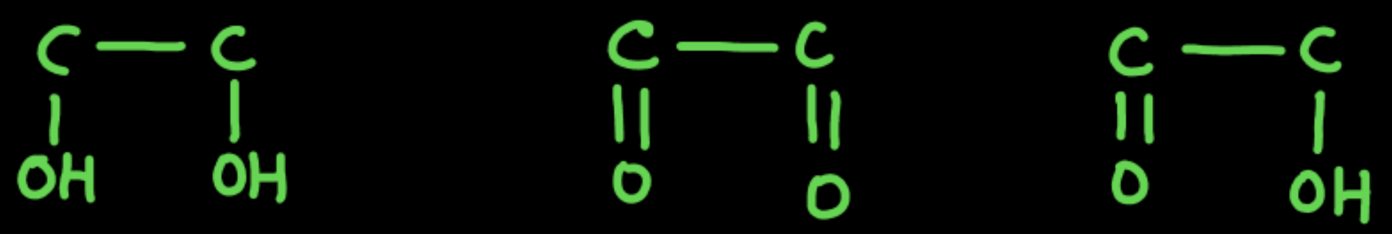
$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - OH \xrightarrow[300^\circ C]{Cu / Ag} CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_3$$

ketone

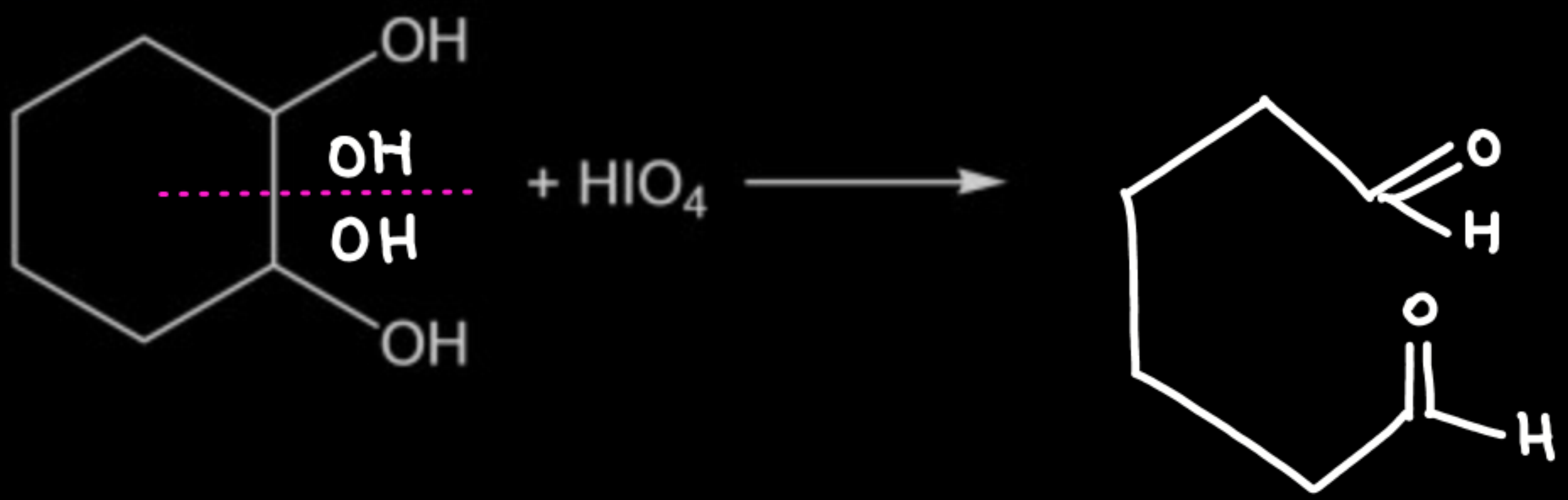
$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH \xrightarrow[300^\circ C]{Cu / Ag} CH_3 - \overset{\overset{CH_2}{\parallel}}{C} - CH_3$$

alkene

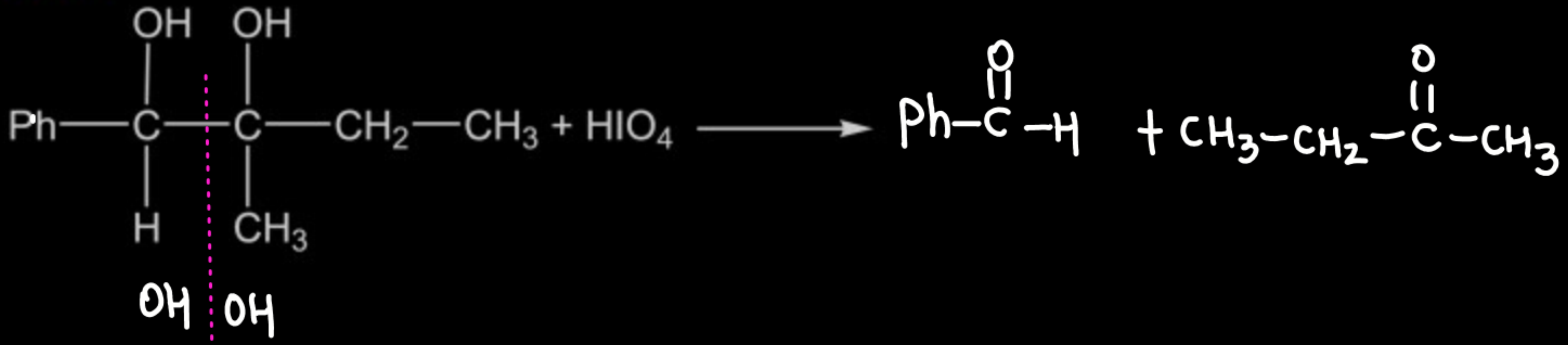
Oxidation of diols.



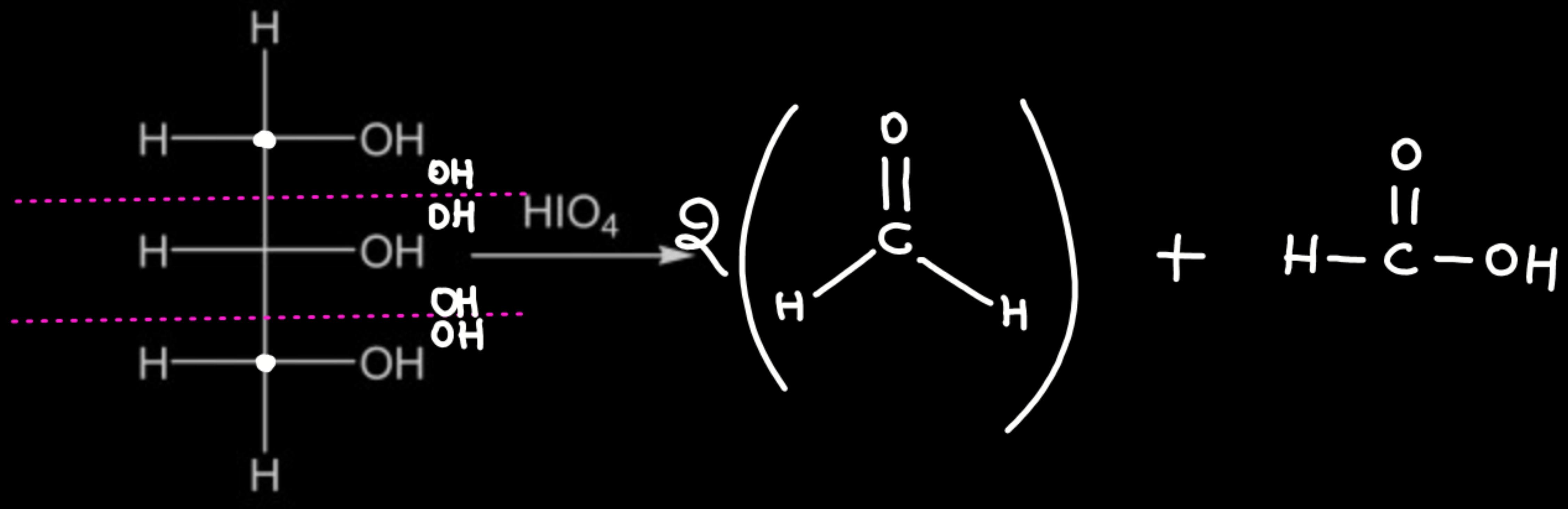
Ques.



Ques.



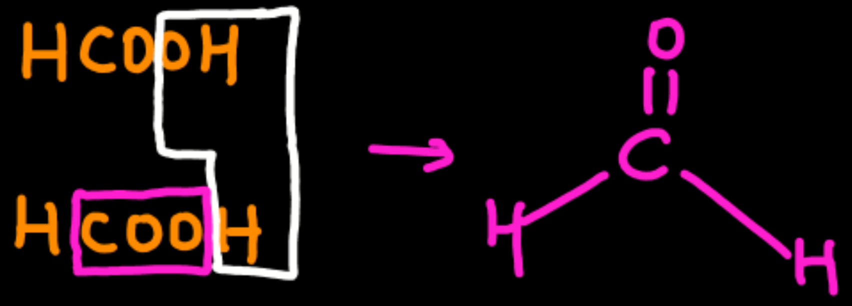
Ques.



(3) Thermal Decomposition of Monocarbonylic Acids: -

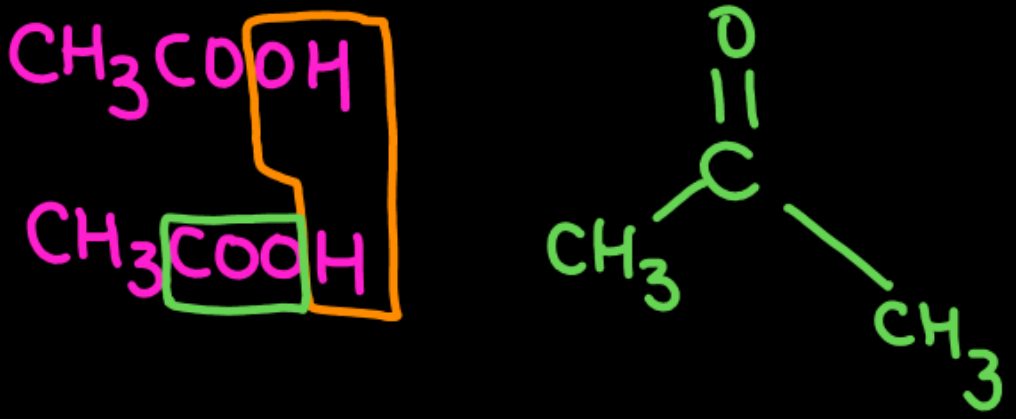
Ques.

$$2HCOOH \xrightarrow[300°C]{MnO}$$



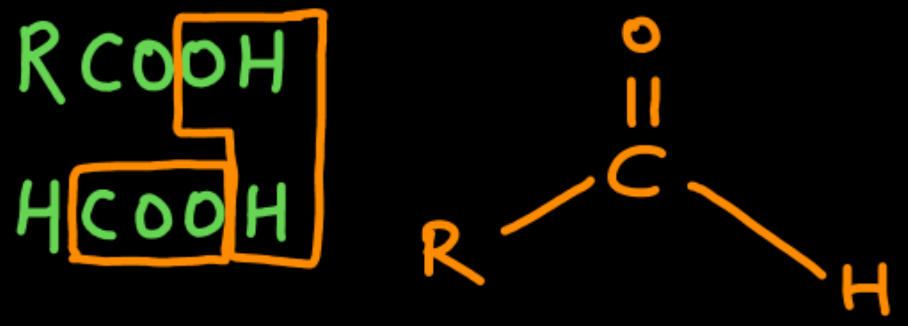
Ques.

$$2CH_3COOH \xrightarrow[300°C]{MnO}$$



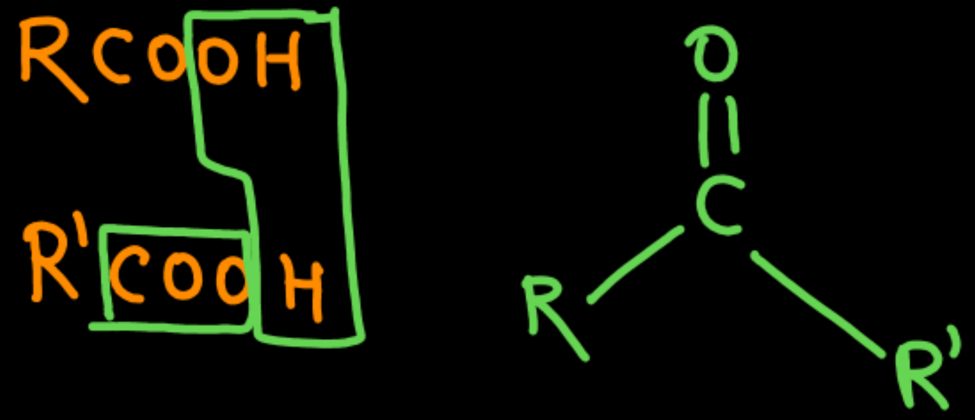
Ques.

$$R-COOH + HCOOH \xrightarrow[300^\circ C]{MnO}$$

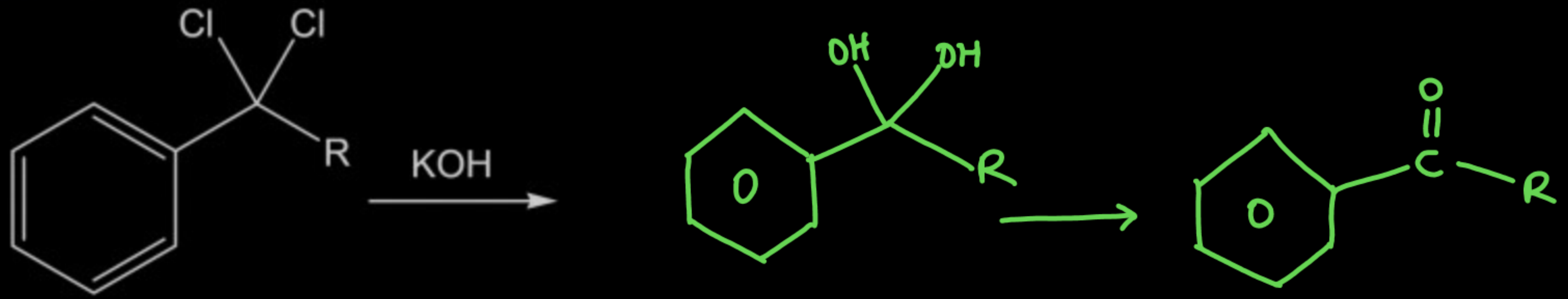


Ques.

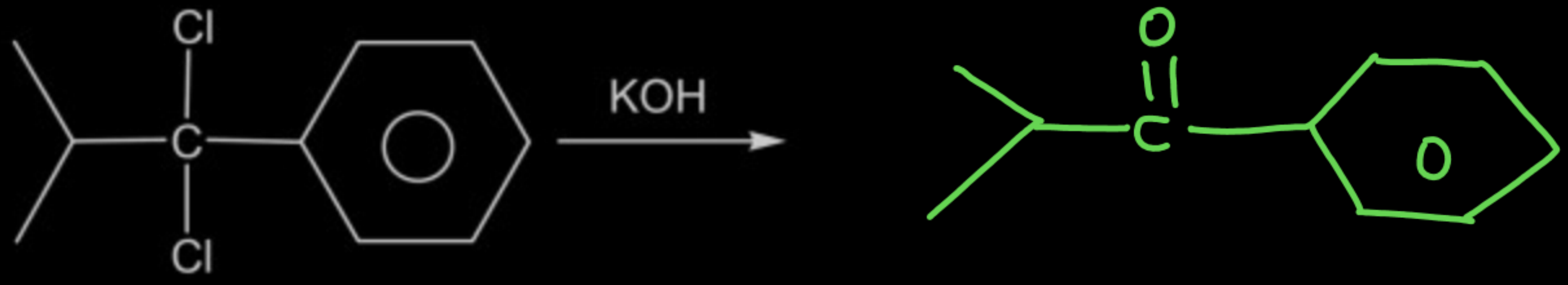
$$RCOOH + R'COOH \xrightarrow[300^\circ C]{MnO}$$



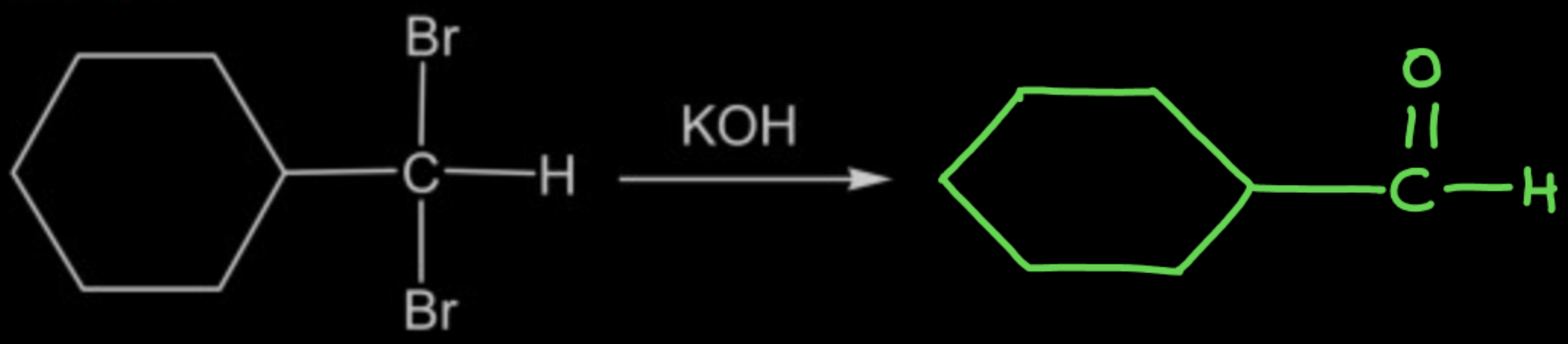
Ques.



Ques.

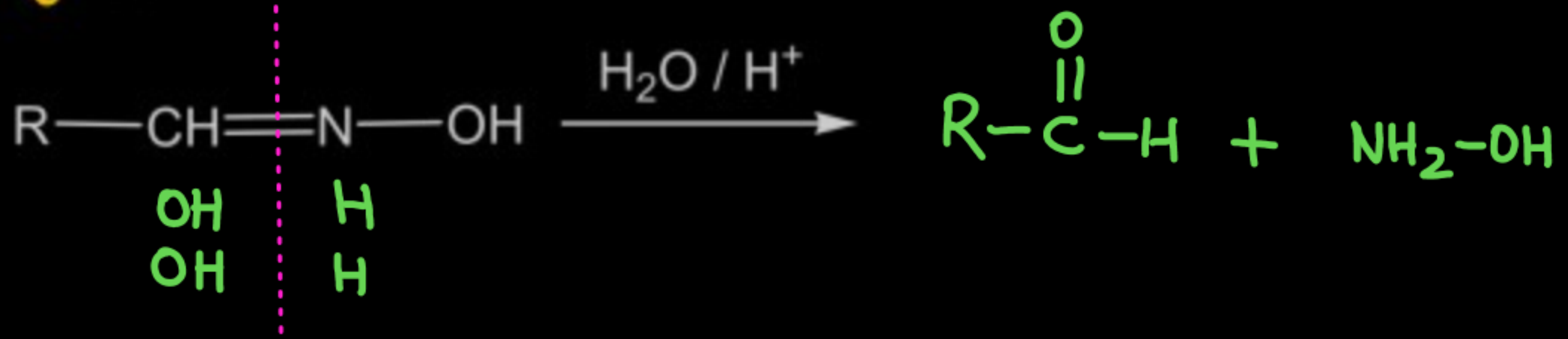


Ques.

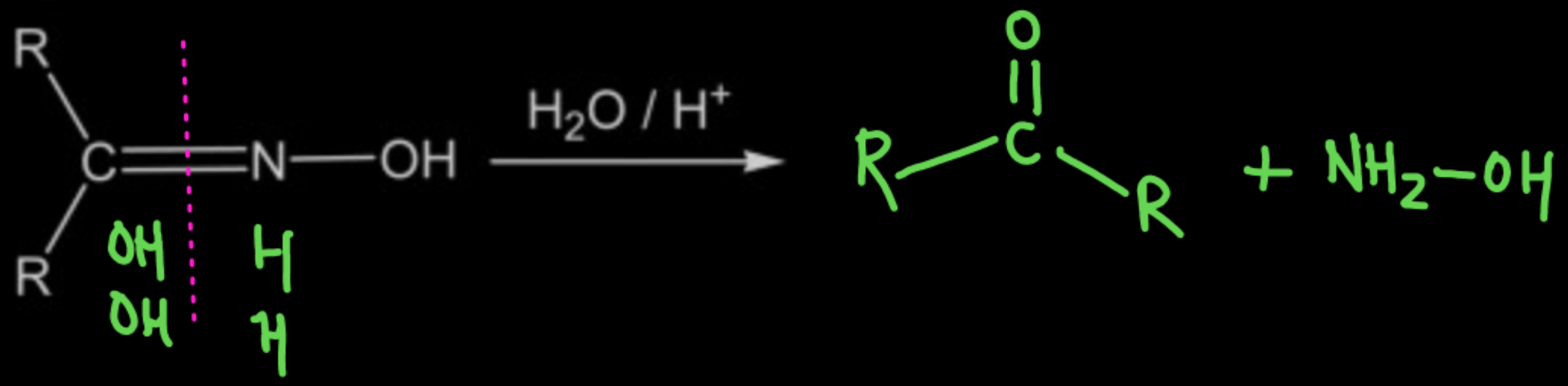


(5) Hydrolysis of Carbonyl Derivatives: -

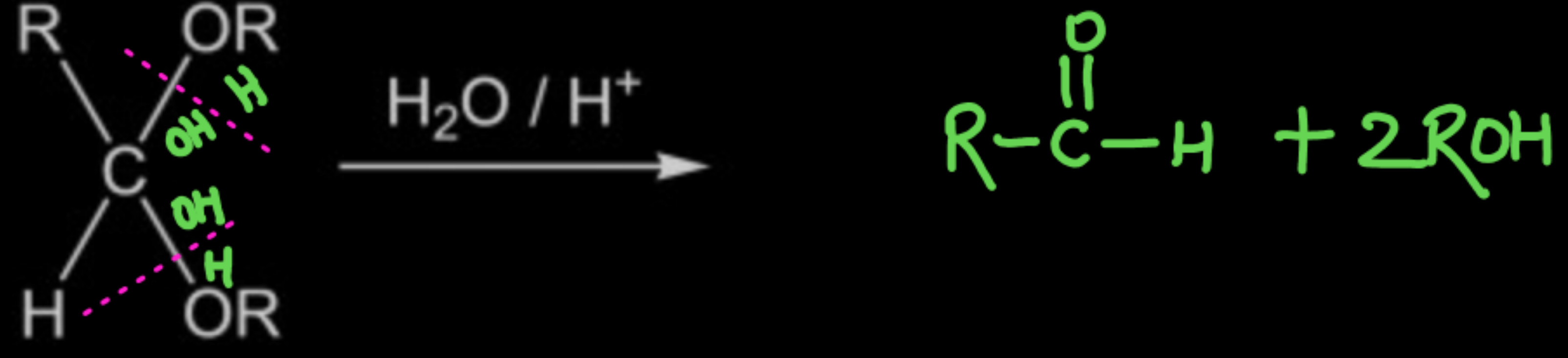
Ques.



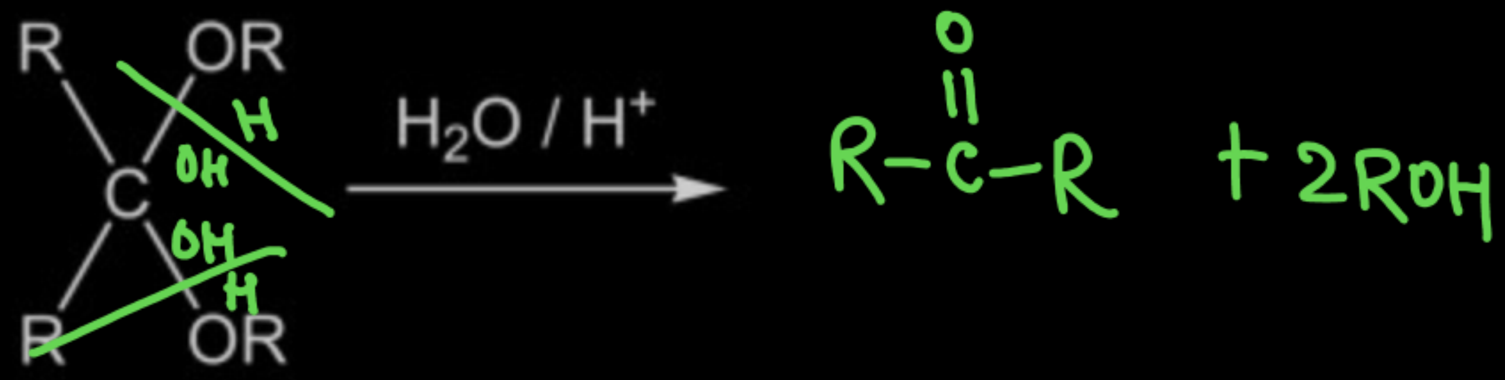
Ques.



Ques.


R
OR
OH
H
C
OH
H
H
OR
H2O / H+
R–C(=O)–H + 2ROH

Ques.


R
OR
H
OH
C
OH
H
R
OR
H2O / H+
R–C(=O)–R + 2ROH

(6) Heating of β-Keto Acids: -

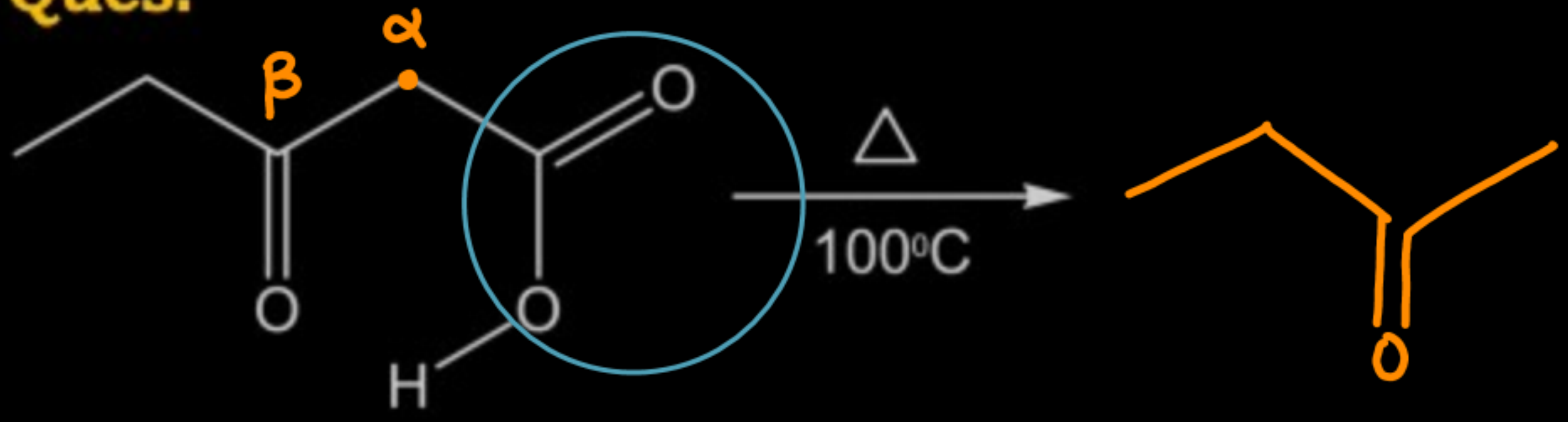
Ques.

$$\underset{\beta}{\overset{\overset{O}{\|}}{H-C}}-\underset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-O-H \xrightarrow[100°C]{\Delta} H-\overset{\overset{O}{\|}}{C}-CH_3$$

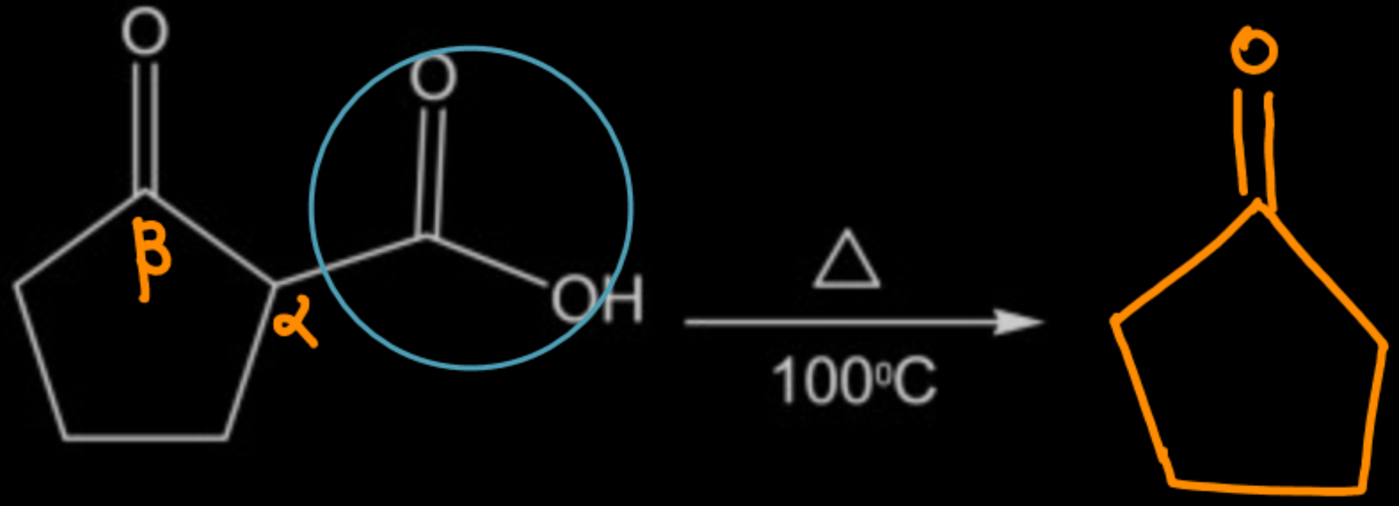
Ques.

$$CH_3-\underset{\beta}{\overset{\overset{O}{\|}}{C}}-\underset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-O-H \xrightarrow[100°C]{\Delta} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Ques.



Ques.



(7) From Grignard Reagent: -

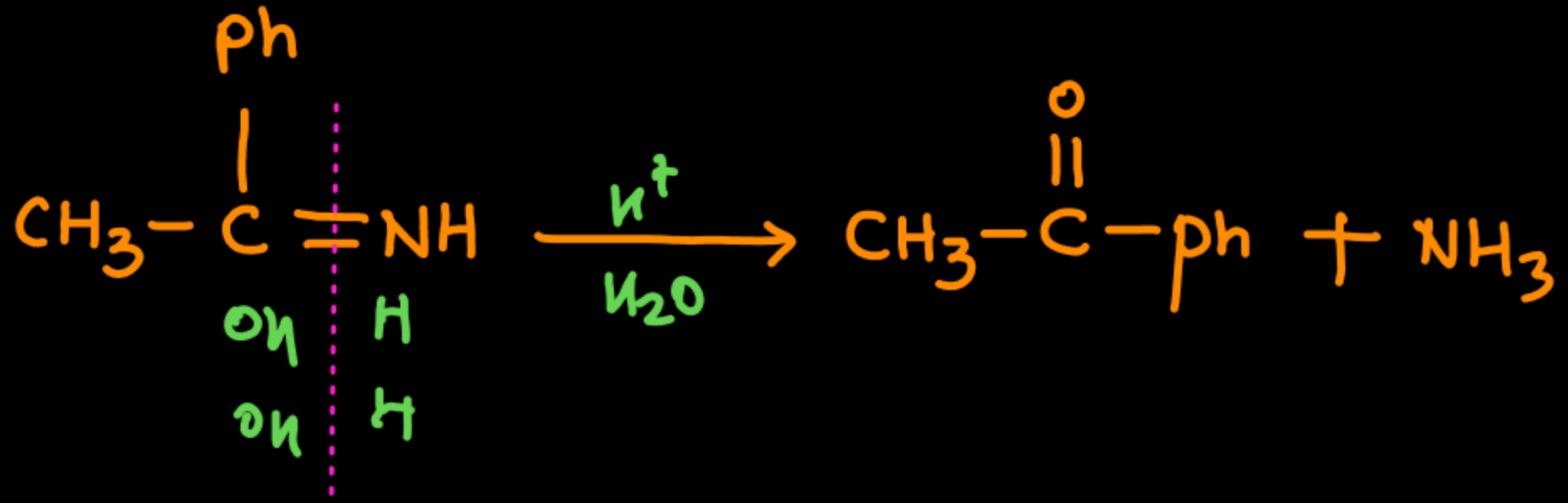
Ques.

$$R-C\equiv N \xrightarrow[H^+ / H_2O]{R'MgCl} R-\underset{\substack{|\\R'}}{C}=NH \xrightarrow[H_2O]{H^+} R-\overset{\substack{O\\||}}{C}-R' + NH_3$$

$$CH_3-C\equiv N \xrightarrow[(ii)\ H^+/H_2O]{(i)\ CH_3MgCl} CH_3-\overset{\substack{CH_3\\|}}{C}=NH \xrightarrow[H_2O]{H^+} CH_3-\overset{\substack{O\\||}}{C}-CH_3 + NH_3$$

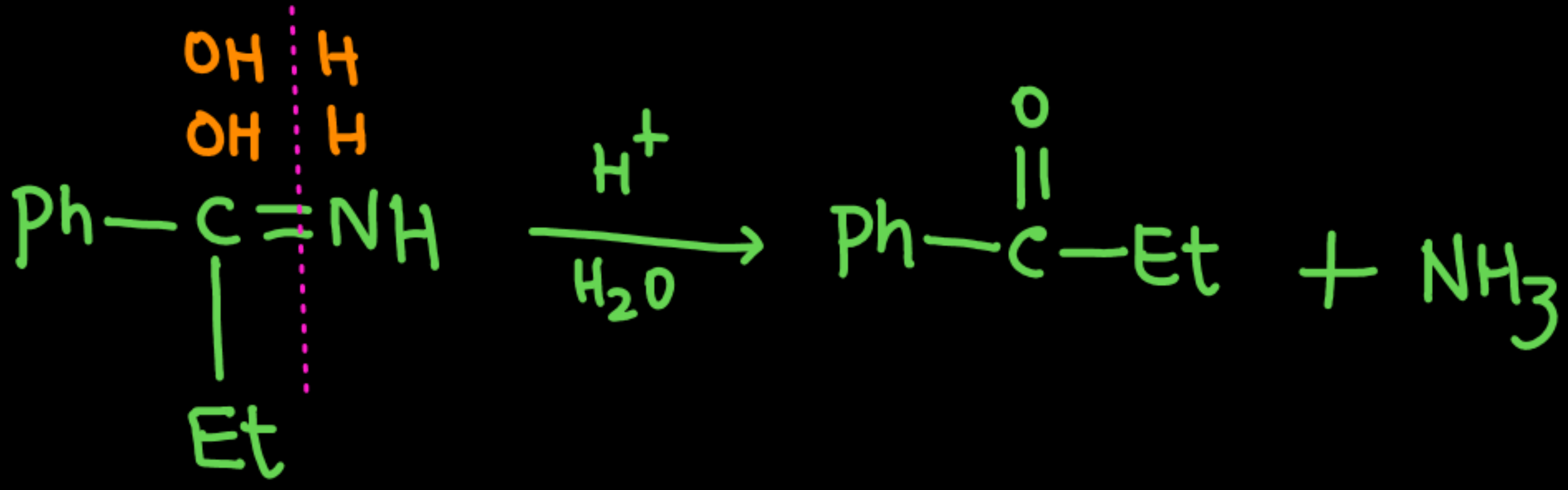
Ques.

$$CH_3 - C \equiv N \xrightarrow[H^+ / H_2O]{Ph\,Mg\,Br}$$



Ques.

$$Ph - C \equiv N \xrightarrow[H^+ / H_2O]{Et\,Mg\,Cl}$$



Method of Preparation Aldehyde Only

① From Acid Halide $\xrightarrow{\text{Reduction}}$ Aldehyde (Rosenmund Catalyst)

② From nitrile (cyanide) $\xrightarrow{\text{Reduction}}$ Aldehyde (i) $SnCl_2 + HCl$ & (ii) Hydrolysis

③ From Ester $\xrightarrow{\text{Reduction}}$ Aldehyde (Using DIBAL H) (ii) DIBAL–H & (ii) Hydrolysis

④ Oxidation of Methyl Benzene $\xrightarrow{\text{Using strong oxidising agent}}$ acid

$\xrightarrow{CrO_2Cl_2}$ Aldehyde

$\xrightarrow{CrO_3}$ Aldehyde

$\xrightarrow[\text{Hydrolysis}]{\text{Side chain chlorination}}$ "

⑤ Gattermann Koch Reaction

⑥ Riemmer Tiemman Reaction

(i) Reduction of Acyl Halide:

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{Quinoline or Sulphur}]{Pd / BaSO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCl$$

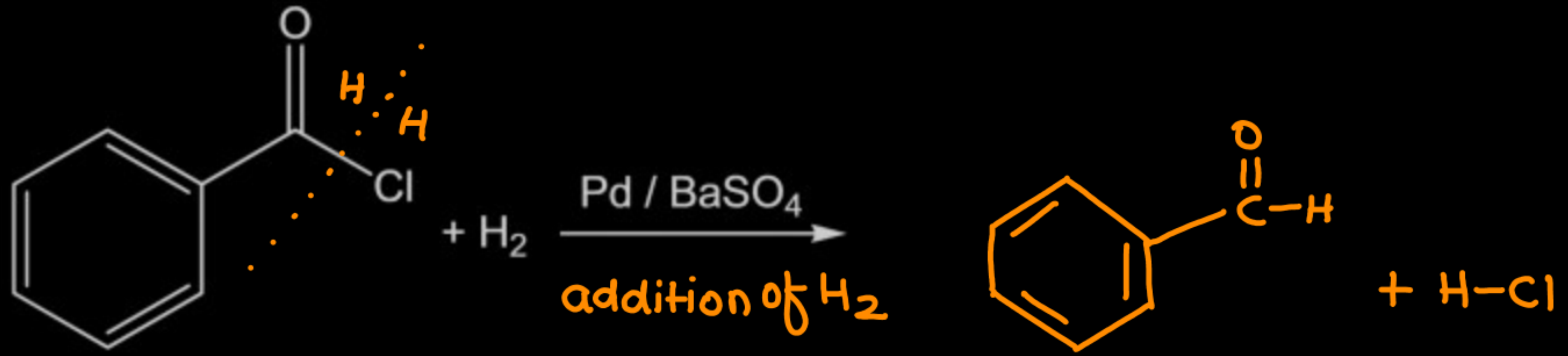
(aldehyde)

Rosenmund Catalyst

→ addition of H_2 ✓

→ Catalytic Hydrogenation

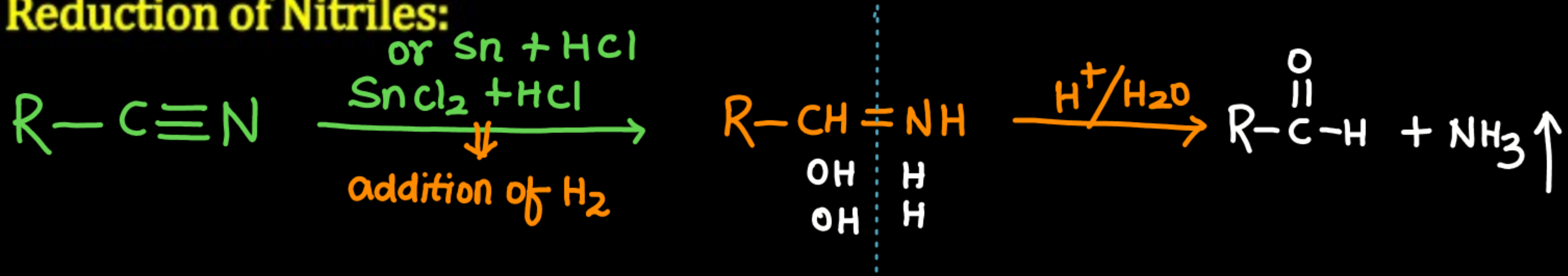
Ques.



Ques.



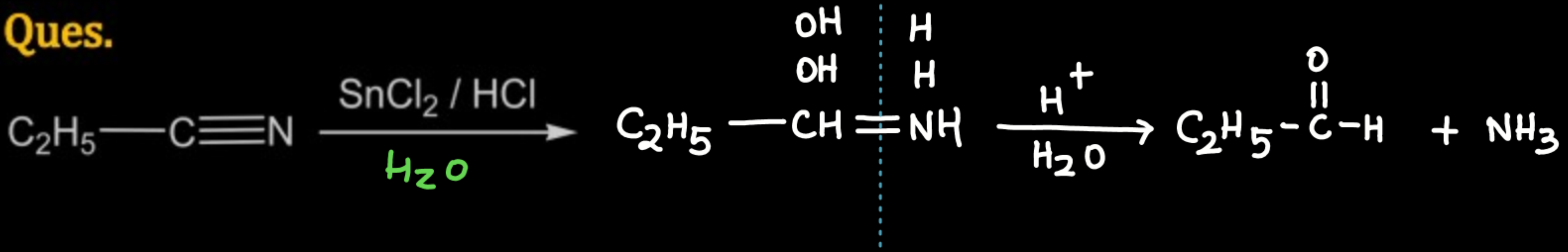
(ii) Reduction of Nitriles:



$SnCl_2 + HCl$

Stephon's Reduction

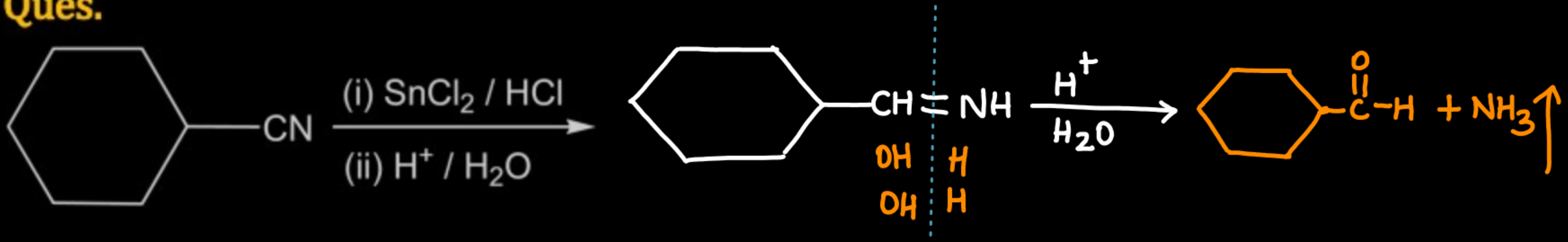
Ques.


$C_2H_5-C\equiv N$
$SnCl_2$ / HCl
H_2O
OH
OH
H
H
$C_2H_5-CH=NH$
H^+
H_2O
$C_2H_5-C(=O)-H$ + NH_3

Ques.

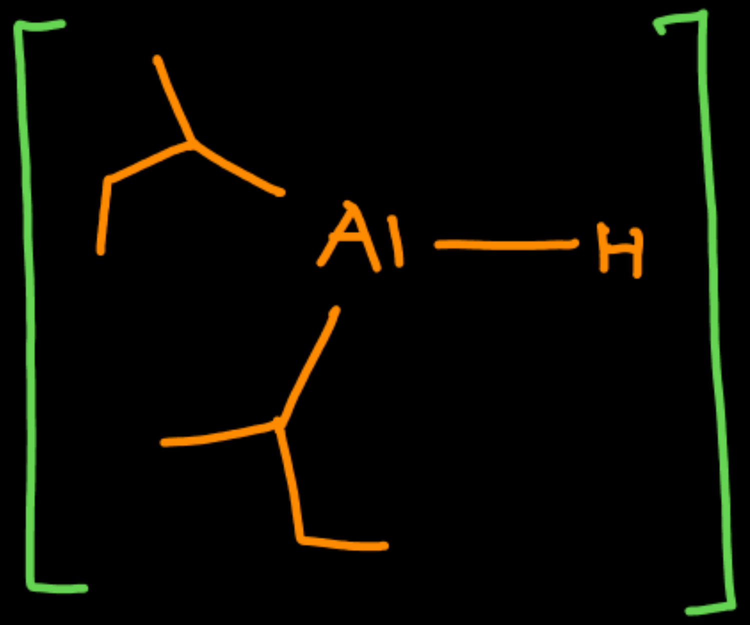

CN
(i) $SnCl_2$ / HCl
(ii) H^+ / H_2O
C≡N
CH=NH
OH
OH
H
H
C–H
O
+NH_3

Ques.



DIBAL – H

Di-Isobutyl Aluminium Hydride



metal Hydride
↓
Release H^-

DIBAL-H

→ **Using DIBAL – H**

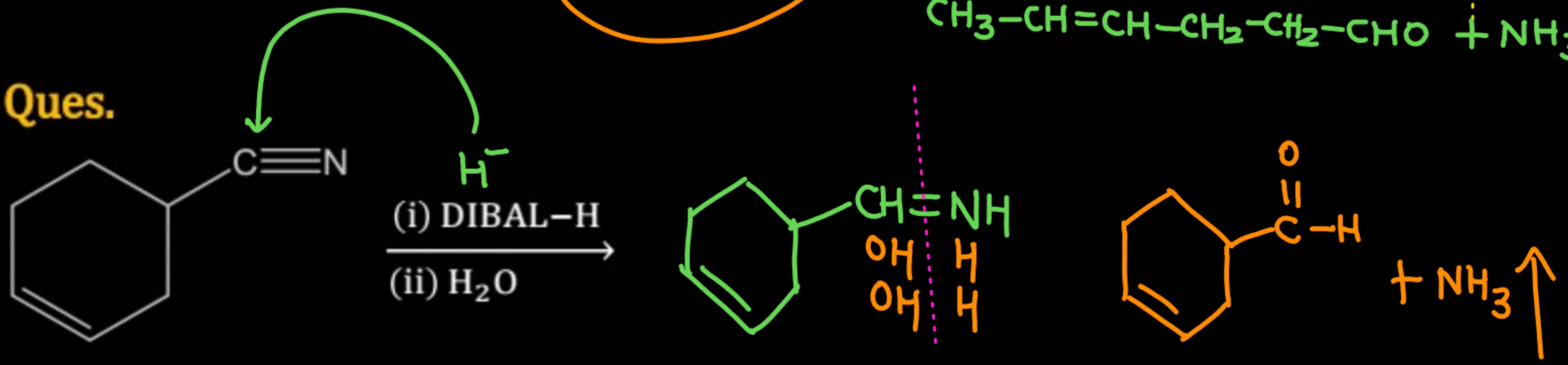
Ques.

$$CH_3 - CH = CH - CH_2 - CH_2 - CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}}$$

$$CH_3 - CH = CH - CH_2 - CH_2 - \overset{\delta+}{C} \equiv \overset{\delta-}{N} \xrightarrow[\text{Gives } H^-]{\text{DIBAL H}} CH_3 - CH = CH - CH_2 - CH_2 - CH = NH$$

$$CH_3 - CH = CH - CH_2 - CH_2 - CHO + NH_3$$

Ques.



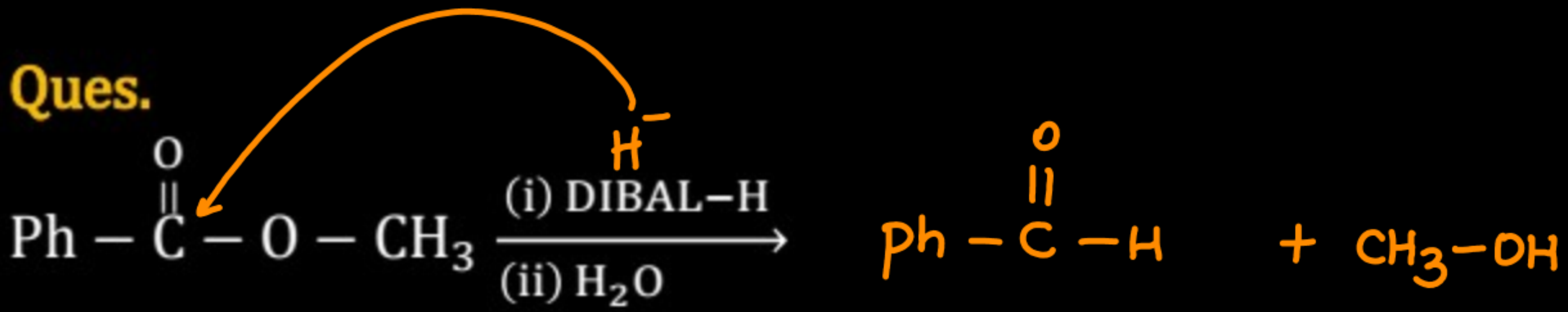
(iii) Reduction of Esters:

Ques.

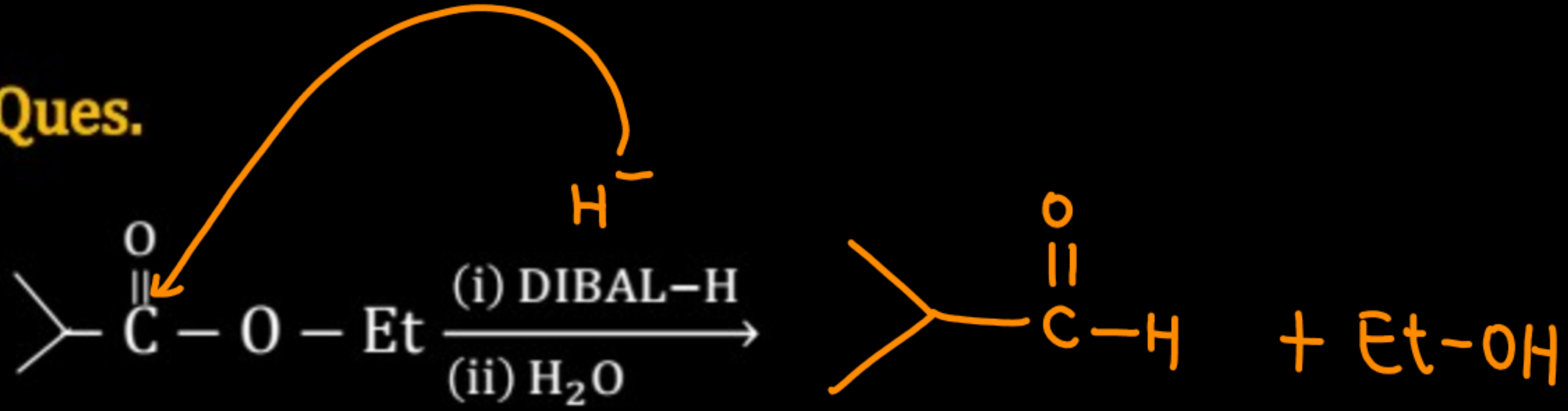
$$CH_3-(CH_2)_2-\overset{\overset{\displaystyle O}{\|}}{\underset{\delta+}{C}}-O-C_2H_5 \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} CH_3-(CH_2)_2-\overset{\overset{\displaystyle O}{\|}}{C}-H + C_2H_5OH$$

H^-

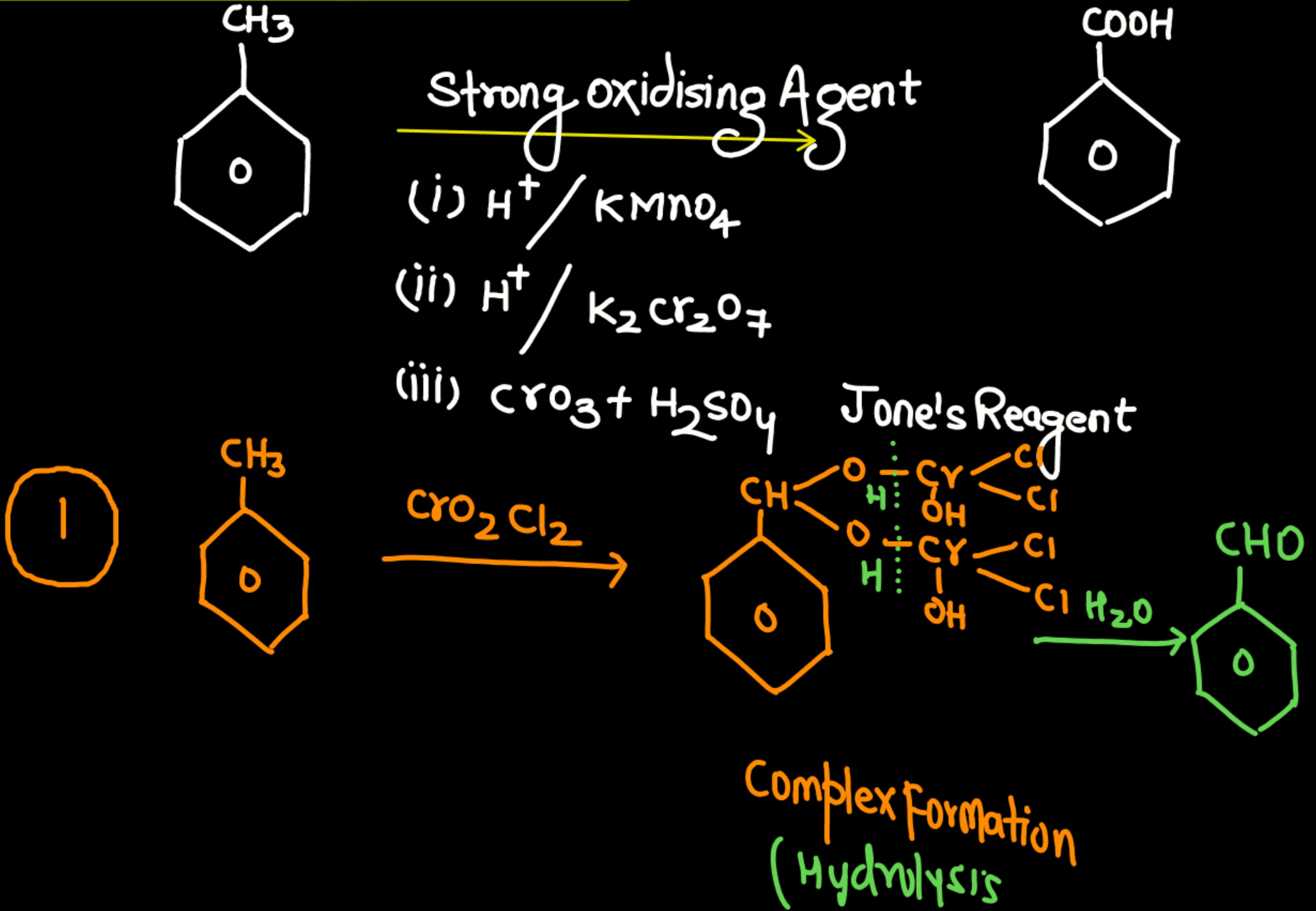
Ques.


H⁻
Ph – C(=O) – O – CH3
(i) DIBAL–H
(ii) H2O
Ph – C(=O) – H + CH3–OH

Ques.

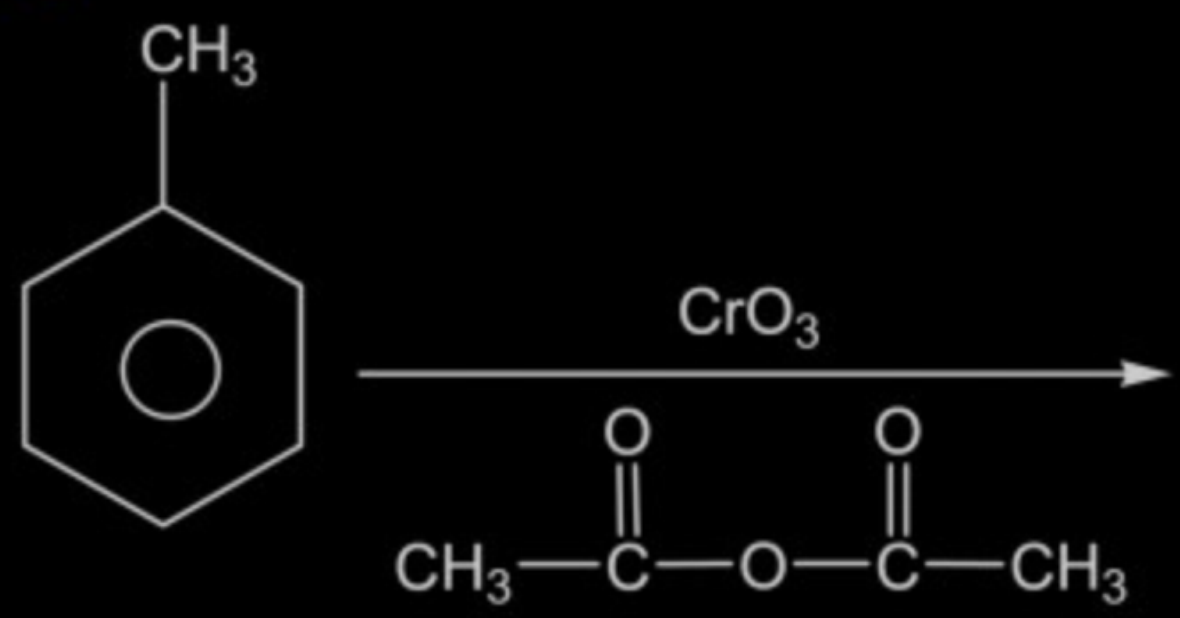

H⁻
C(=O) – O – Et
(i) DIBAL–H
(ii) H2O
C(=O)–H + Et-OH

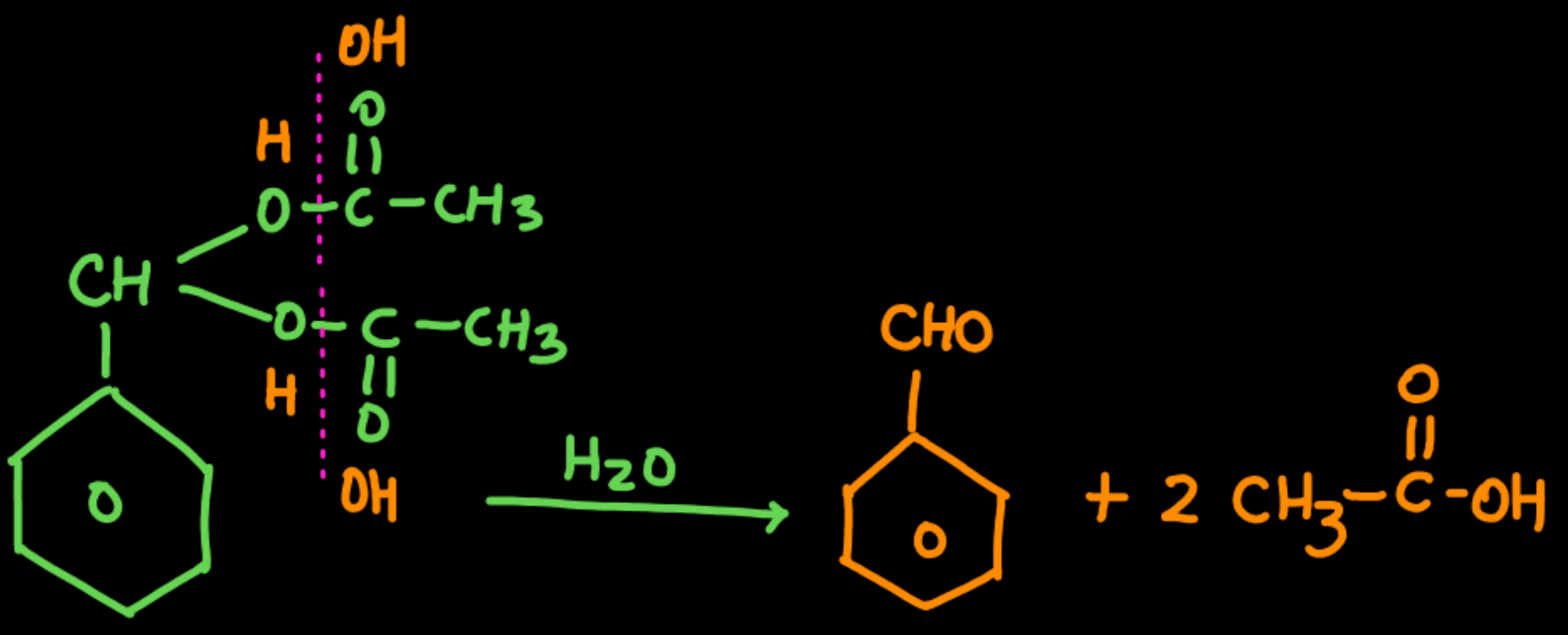
Oxidation of Methyl Benzene: -



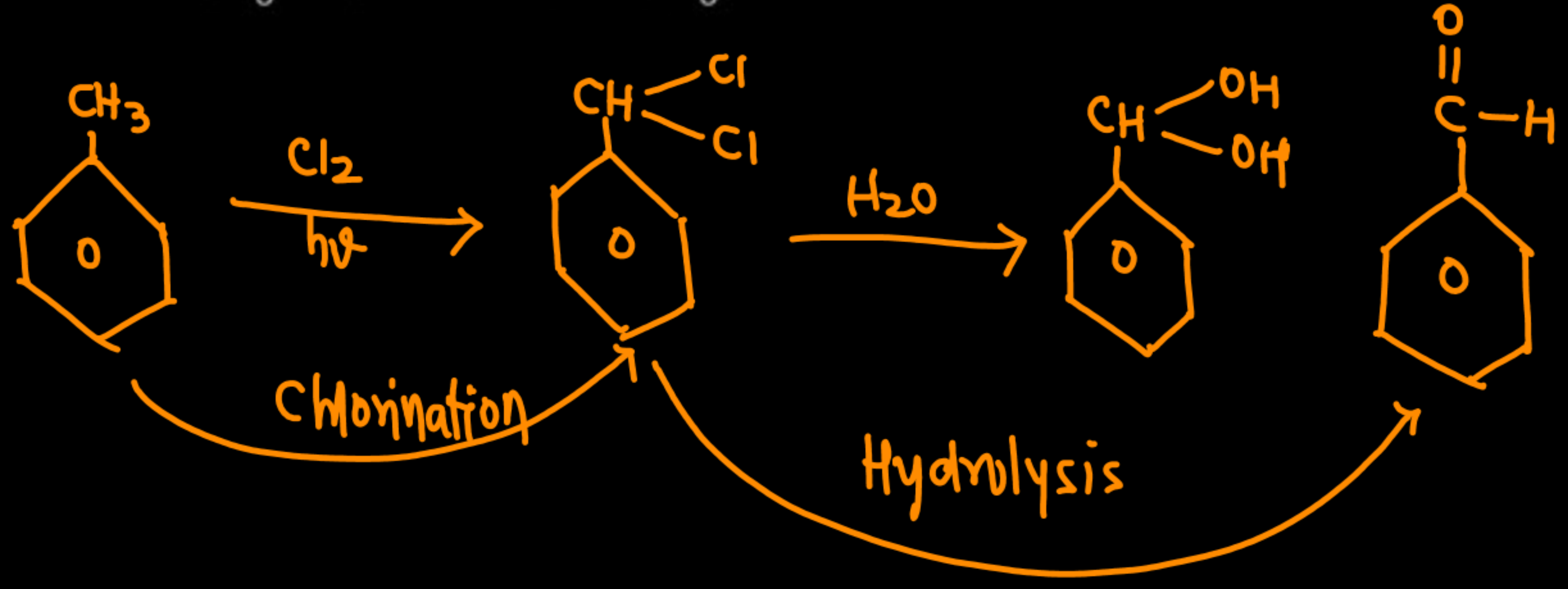
(b) By using chromic oxide (CrO_3):

Ques.

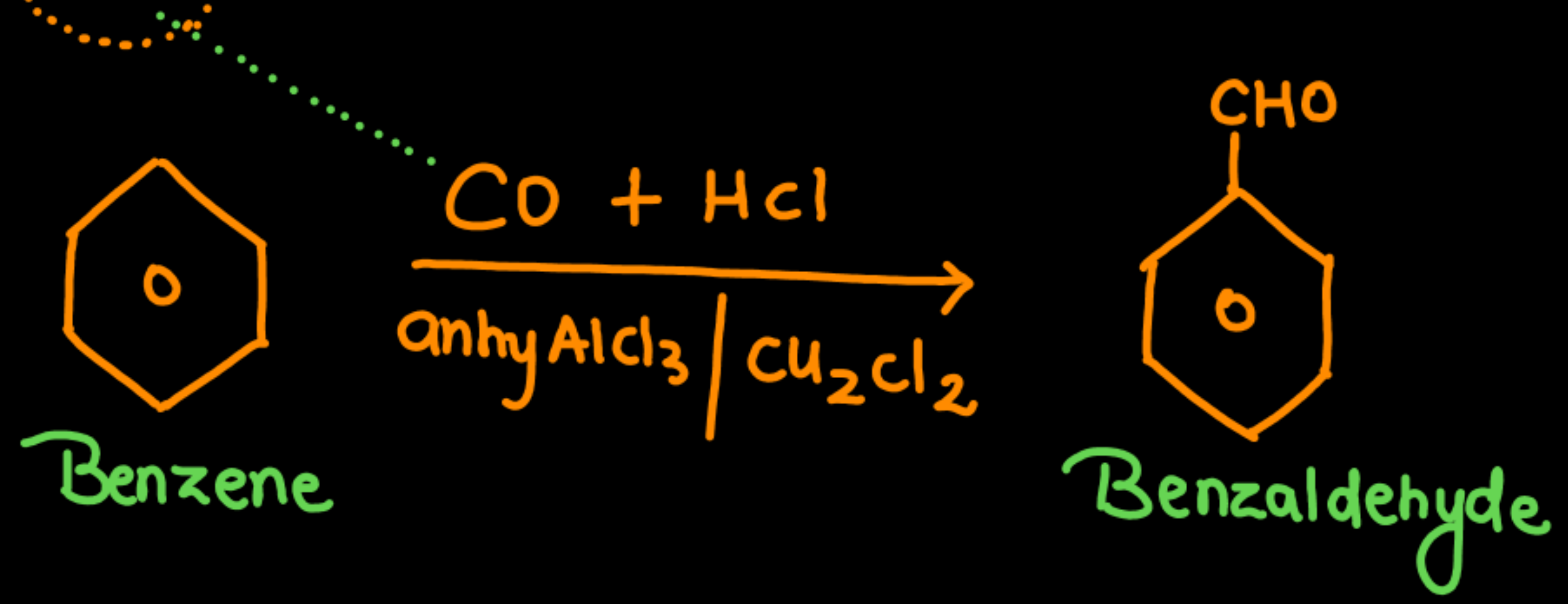




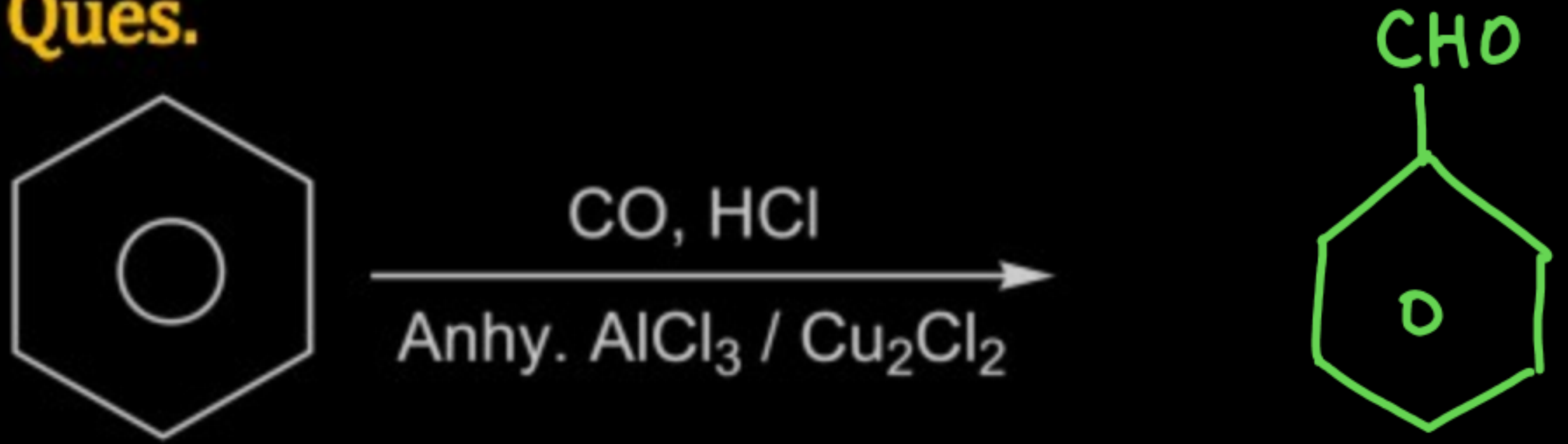
(c)



By Gatterman – Koch reaction: -

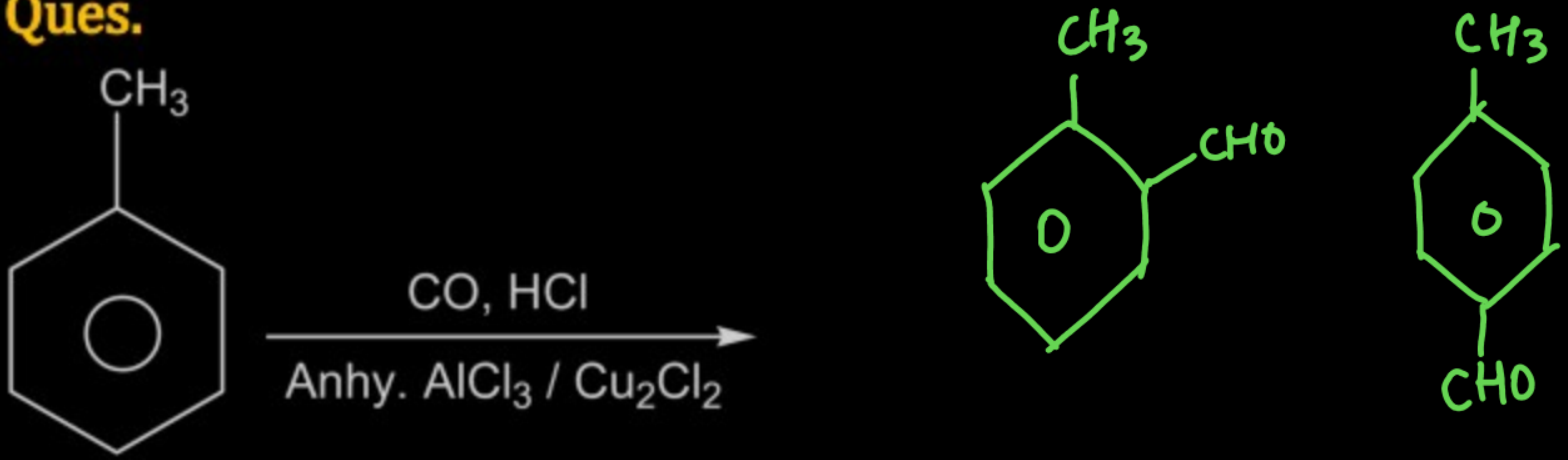


Ques.



CO, HCl
Anhy. $AlCl_3$ / Cu_2Cl_2
CHO

Ques.



CH_3
CO, HCl
Anhy. $AlCl_3$ / Cu_2Cl_2
CH_3
CHO
CH_3
CHO

Preparation of Ketone only

(i) Using Grignard Reagent $RMgX$

(ii) Using R_2Cd (dialkyl Cadmium)

(iii) Using Gilmann Reagent R_2CuLi

} Organometallic Comp

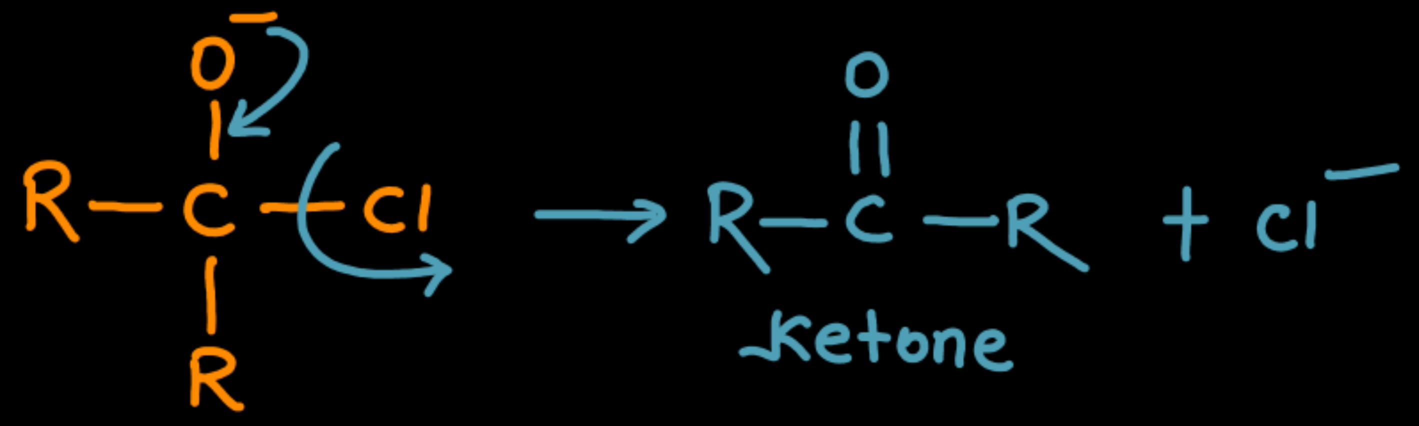
↳ Releases R^-

(1) From Grignard Reagent: -

Ques.

$$\overset{-}{R}\overset{+}{Mg}\overset{+}{X}^{-} + R - \overset{\overset{\large O}{\|}}{C} - Cl \xrightarrow{H_2O}$$

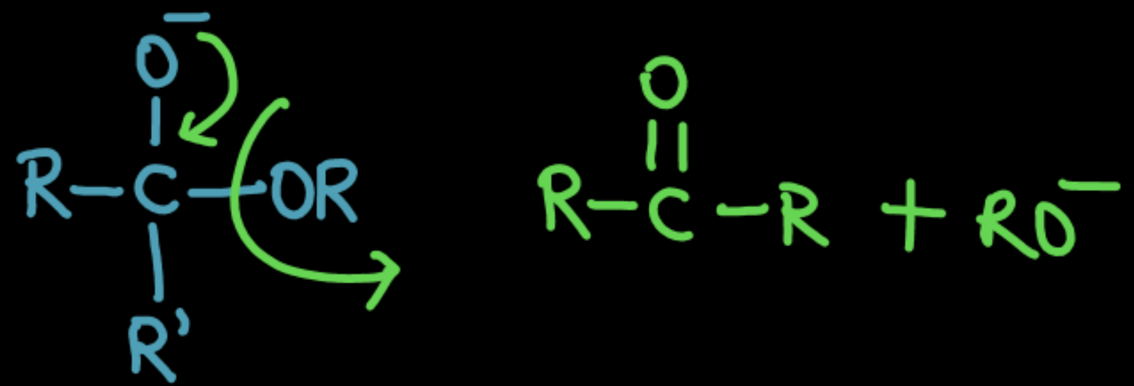




Ques.

$$R'MgX + R - \overset{\overset{\large O}{\|}}{C} - OR \xrightarrow{H_2O}$$

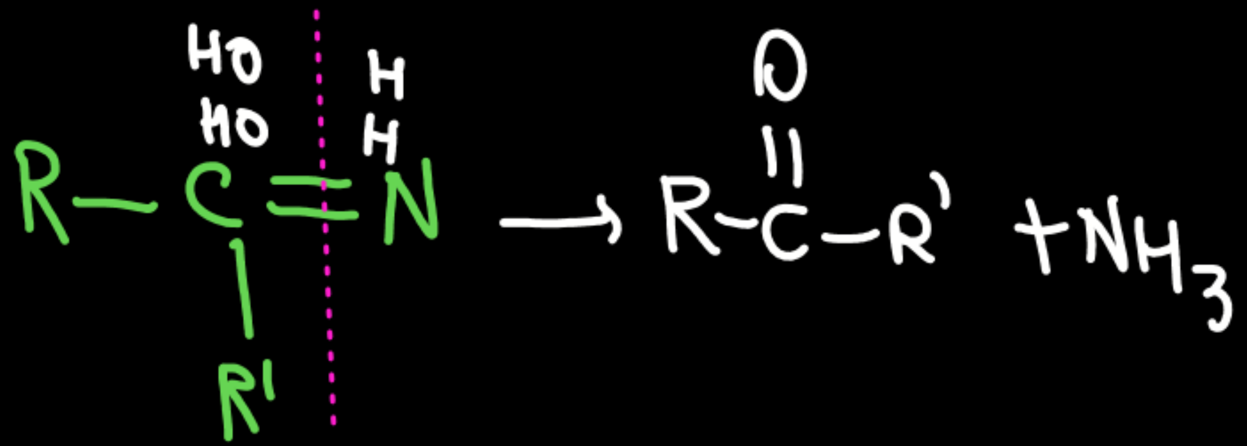




Ques.

$$R'MgX + R - C \equiv N \xrightarrow{H_2O}$$





(2) From Acyl Chloride & Dialkyl Cadmium: -

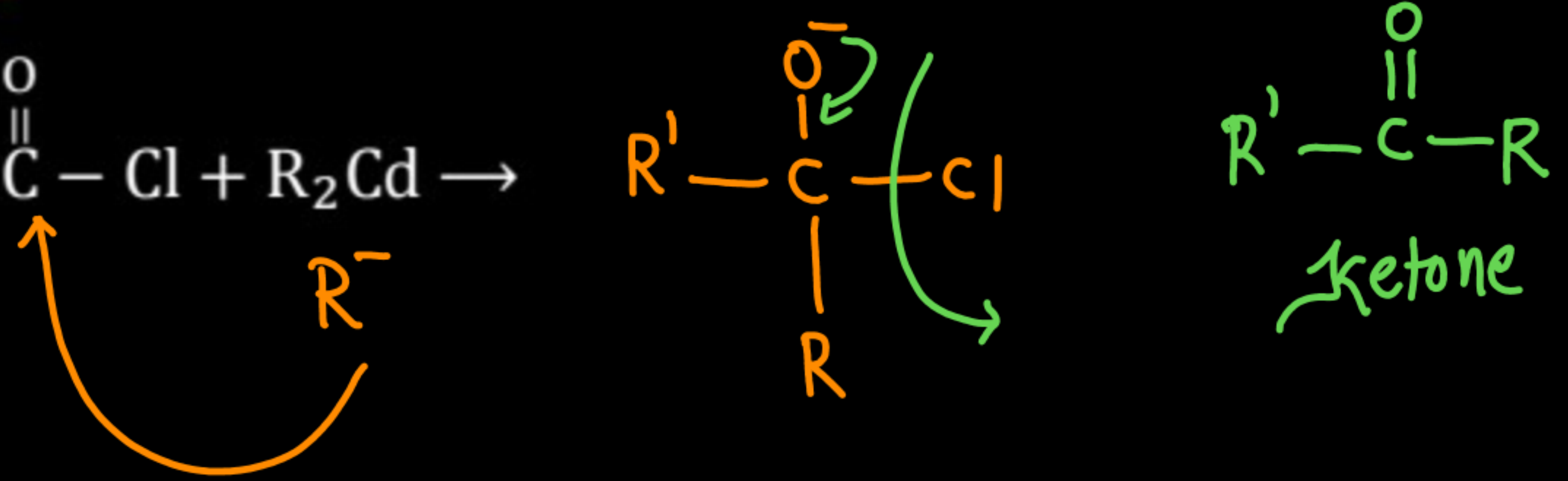
Ques.

$$2R-Mg-X+\overset{+2}{CdCl_2}\longrightarrow R_2Cd$$

$$R_2Cd \downarrow R^-$$

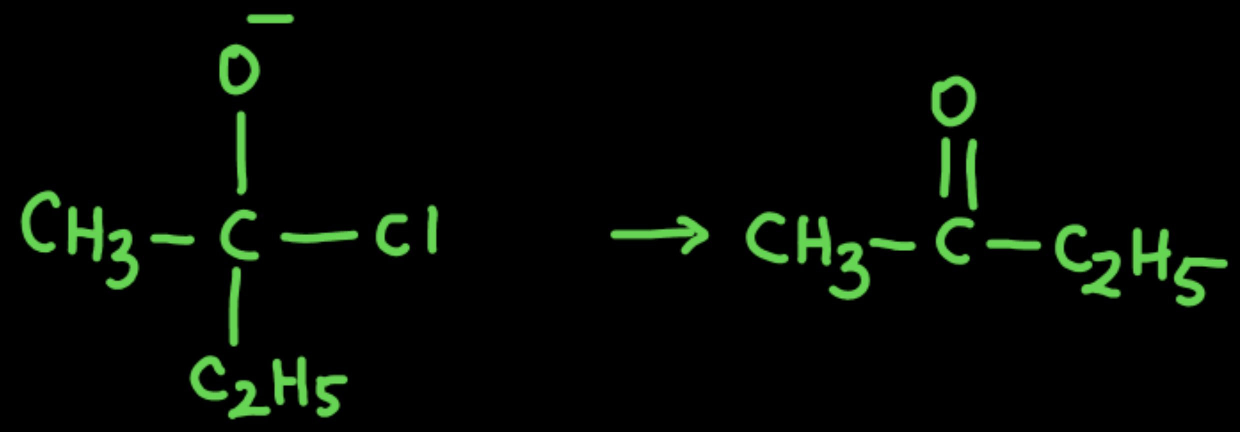
Ques.

$$R'-\overset{\overset{O}{\|}}{C}-Cl+R_2Cd\longrightarrow$$



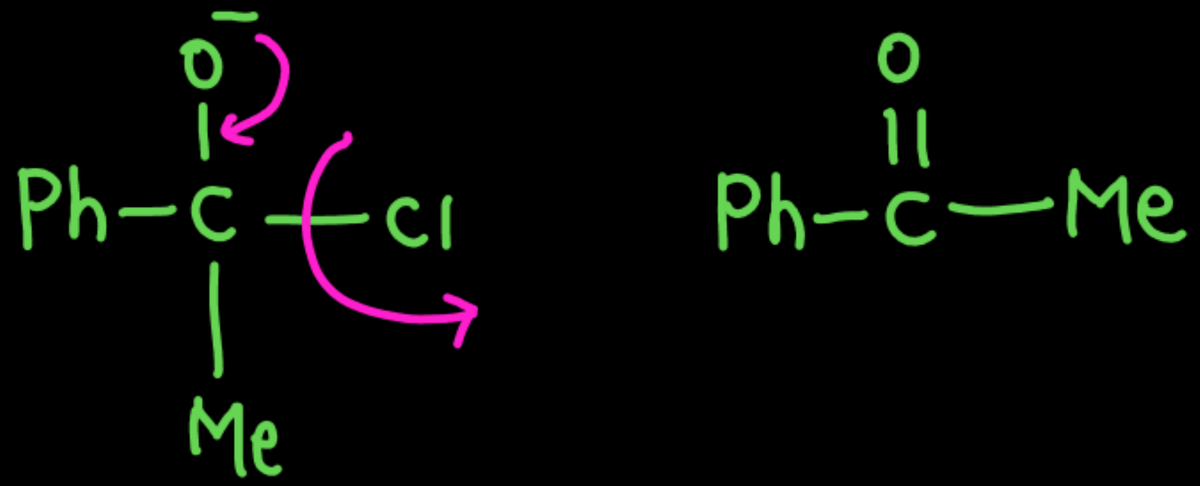
Ques.

$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl+(C_2H_5)_2Cd\longrightarrow$$



Ques.

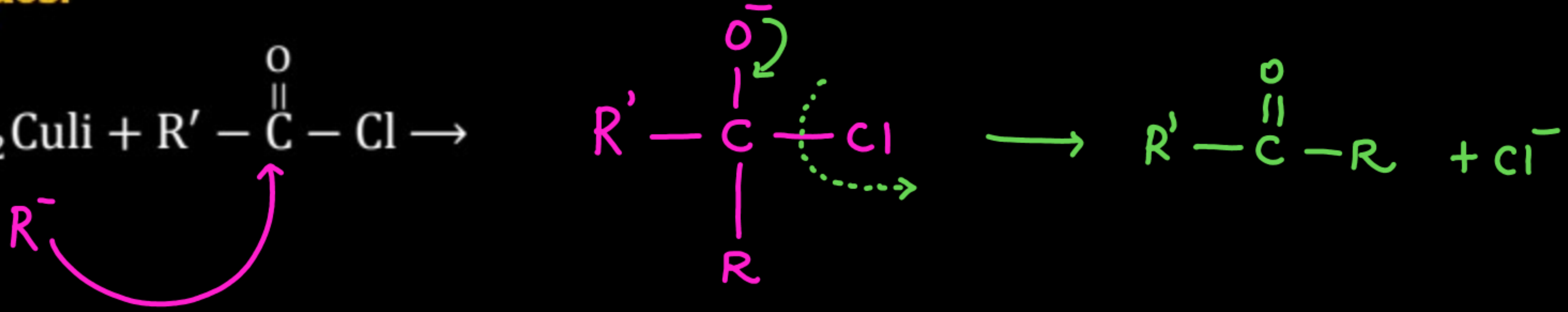
$$2Ph-\overset{\overset{\displaystyle O}{\|}}{C}-Cl+(Me)_2Cd\longrightarrow$$



(3) From R_2CuLi (Gilmann Reagent): -

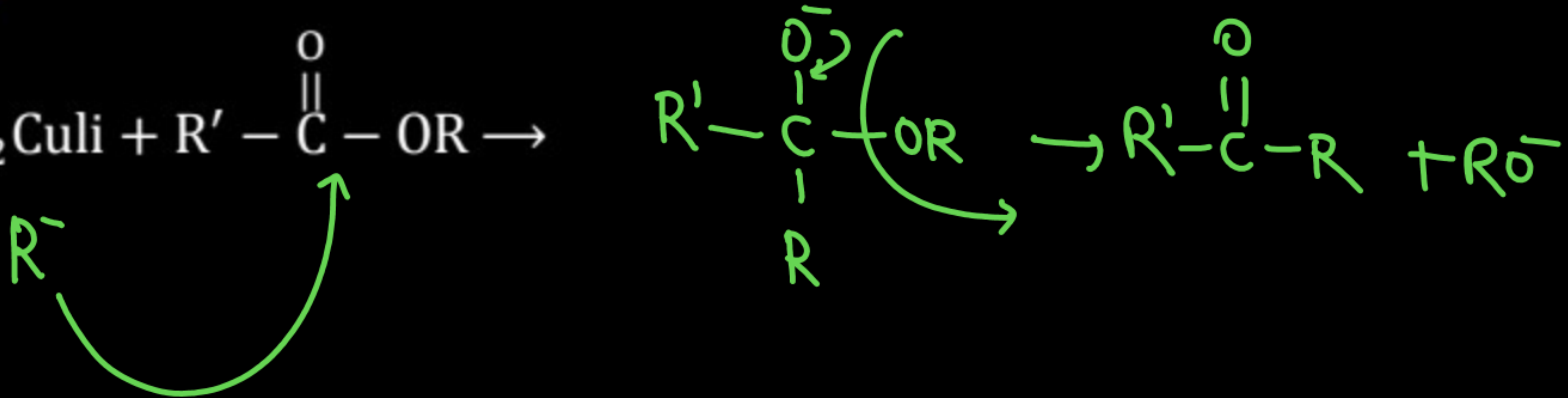
Ques.

$$R_2CuLi + R' - \overset{\overset{\displaystyle O}{\|}}{C} - Cl \longrightarrow$$



Ques.

$$R_2CuLi + R' - \overset{\overset{\displaystyle O}{\|}}{C} - OR \longrightarrow$$



Ques.

$$(CH_3)_2CuLi + Et-\overset{\overset{\large O}{\|}}{C}-Cl \longrightarrow \quad Et-\overset{\overset{\large O}{\|}}{C}-CH_3$$

CH_3^-

Ques.

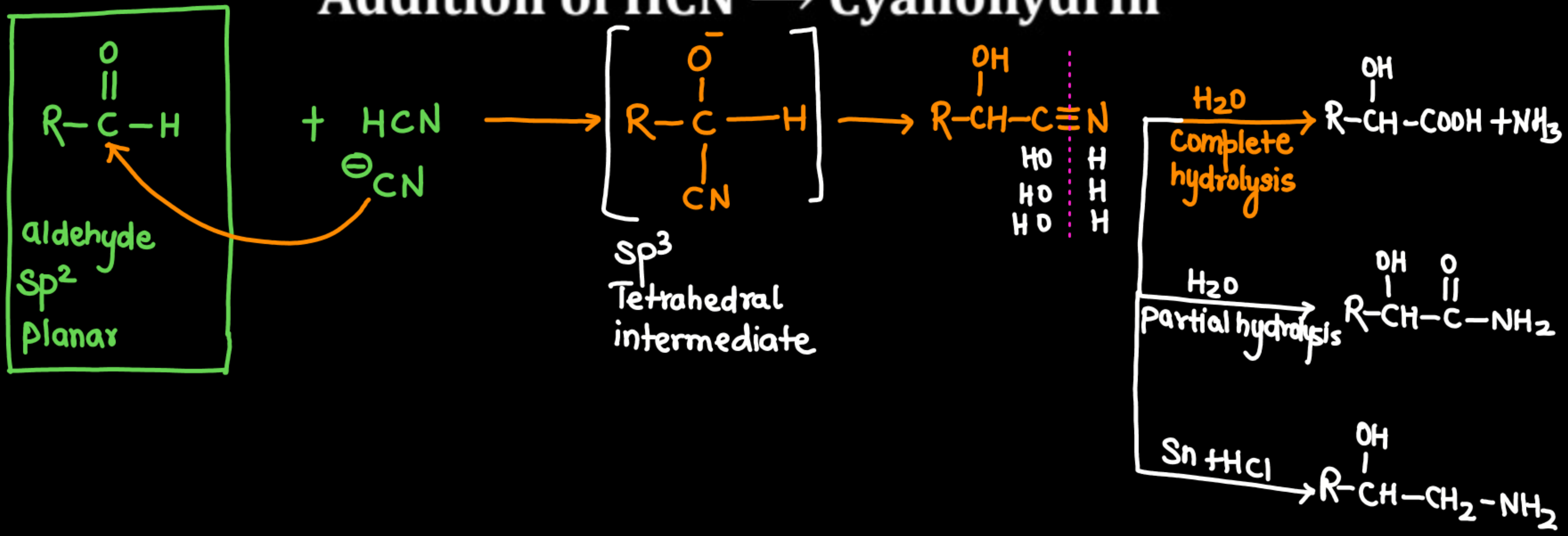
$$(Ph)_2CuLi + CH_3-\overset{\overset{\large O}{\|}}{C}-\underline{OR'} \longrightarrow \quad CH_3-\overset{\overset{\large O}{\|}}{C}-Ph$$

Ph^-

Chemical Properties

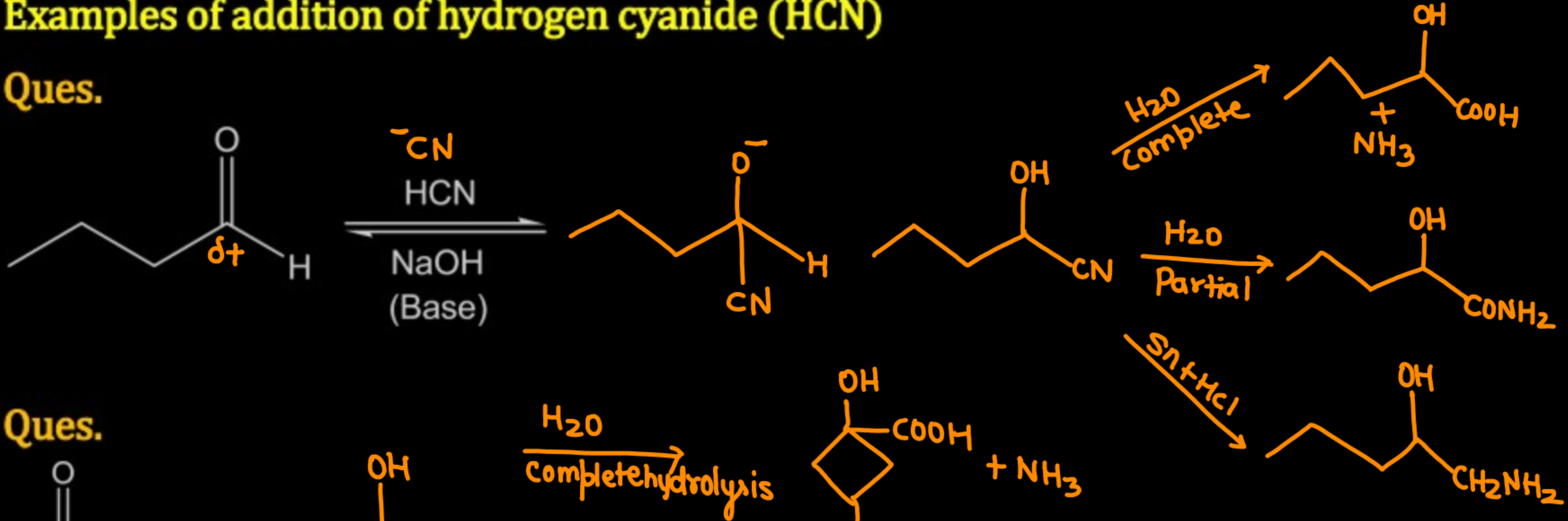
1. Addition of HCN
2. Addition of $NaHSO_3$ (Sodium bisulphite)

Addition of HCN ⟶ Cyanohydrin

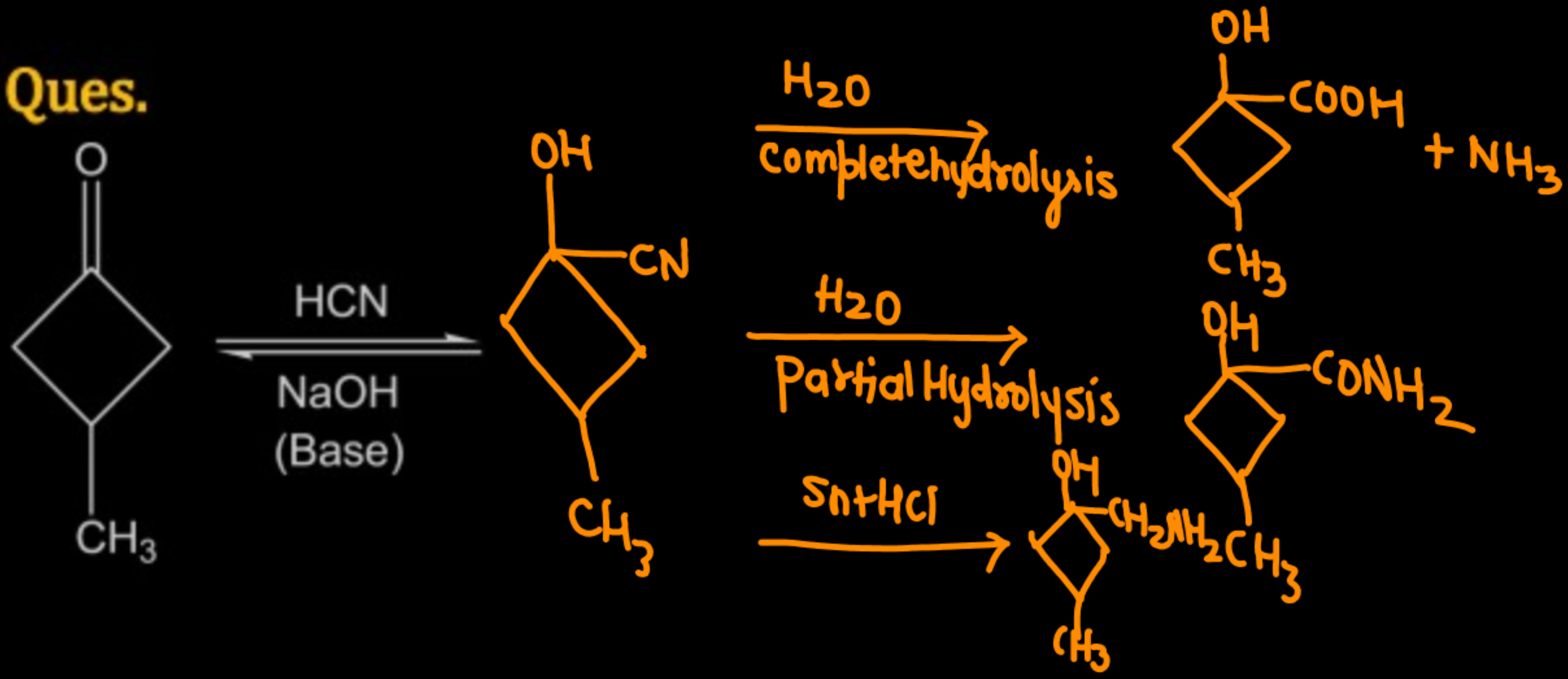


Examples of addition of hydrogen cyanide (HCN)

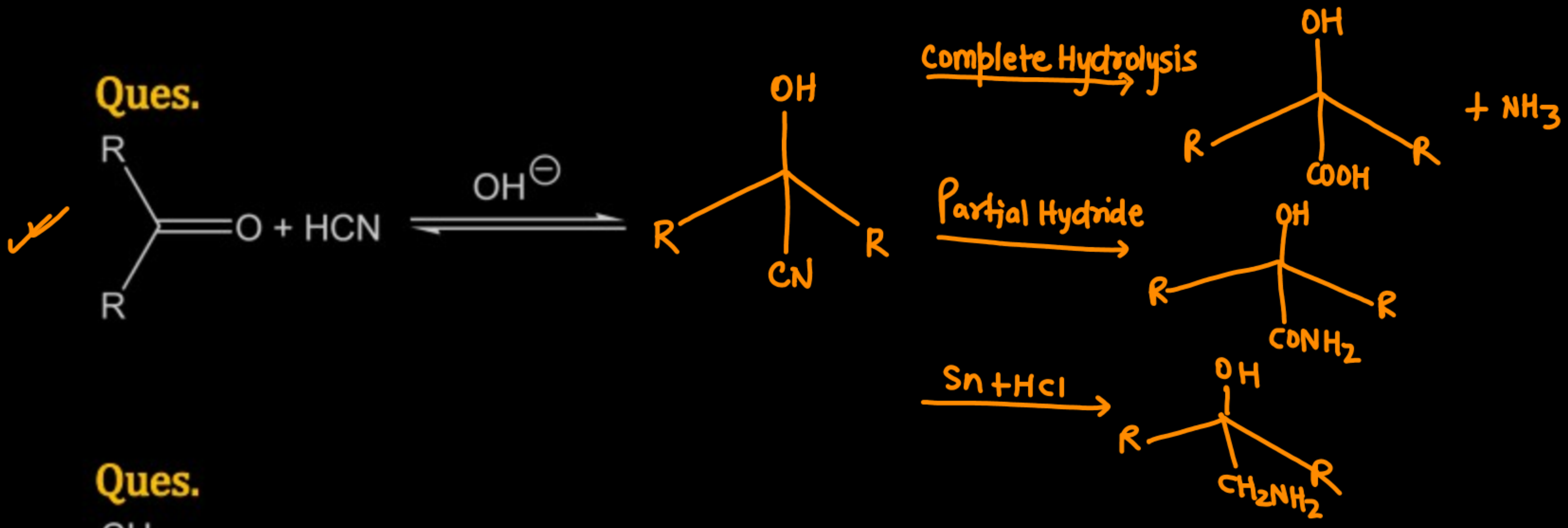
Ques.



Ques.

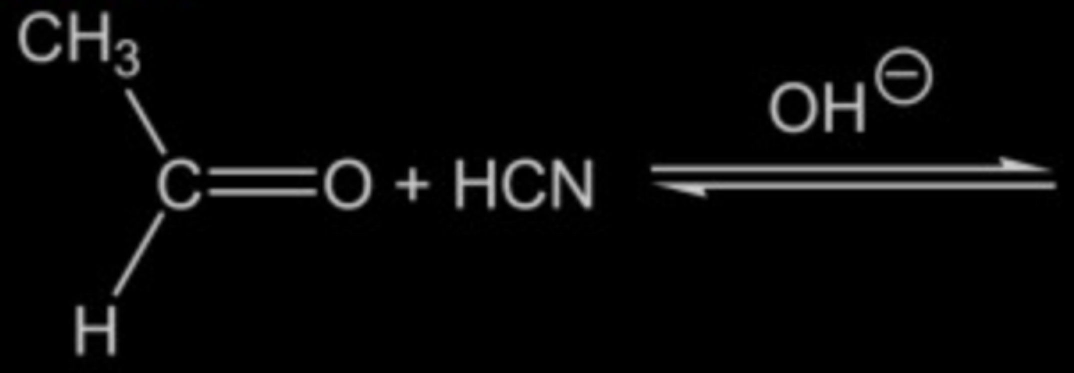


Ques.



R
R
O + HCN
OH⊖
OH
CN
R
R
Complete Hydrolysis
OH
COOH
R
R
+ NH3
Partial Hydride
OH
CONH2
R
R
Sn + HCl
OH
CH2NH2
R
R

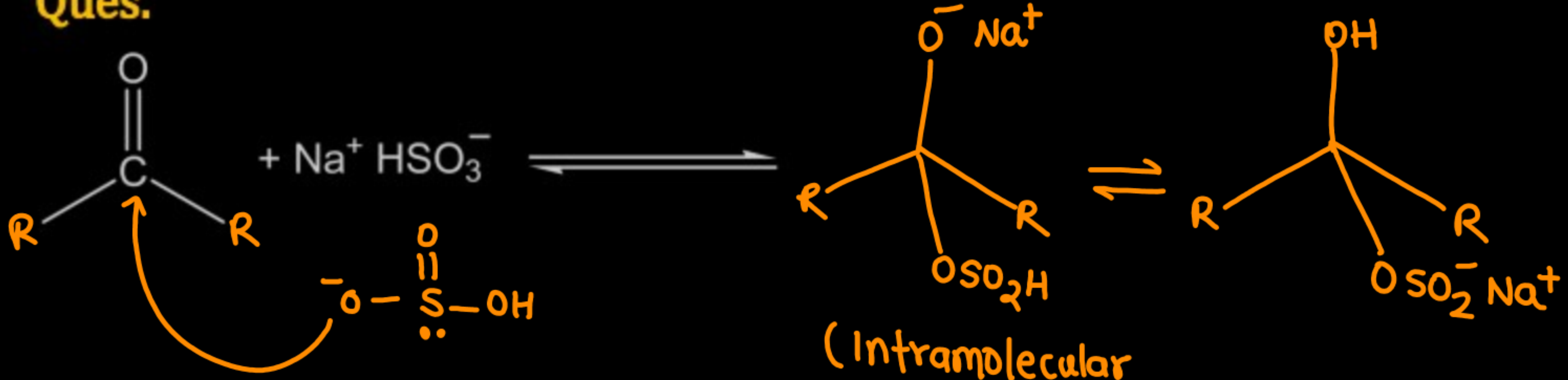
Ques.



CH3
C
O + HCN
H
OH⊖

(2) Addition of Sodium Bisulphite ($NaHSO_3$)

Ques.



(Intramolecular proton transfer)

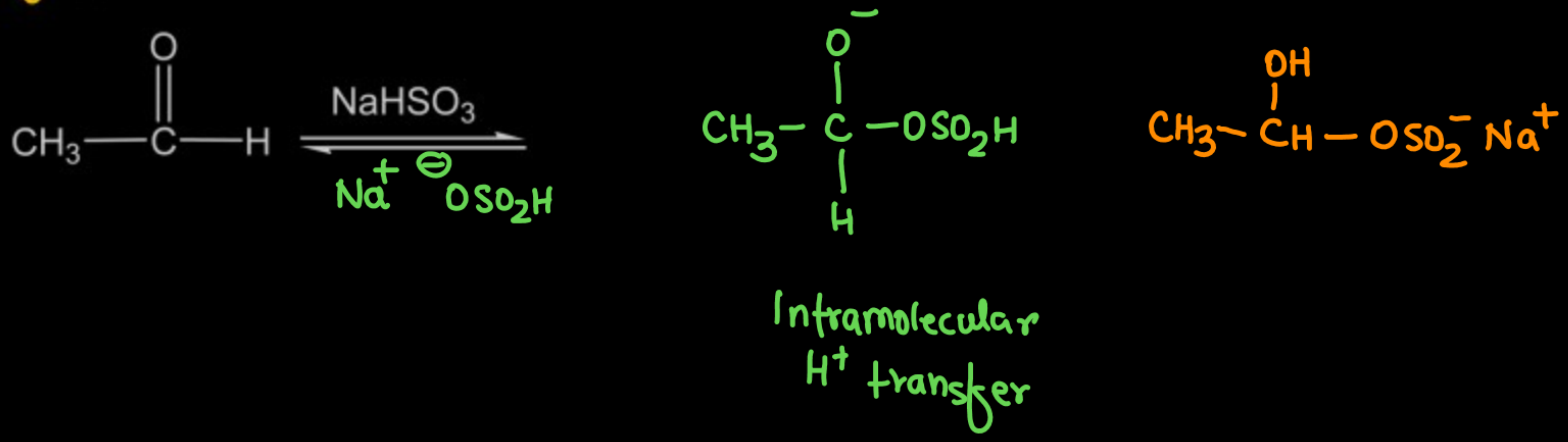
↓

bcoz Solvent is not present.

This reaction is used in purification of aldehyde.

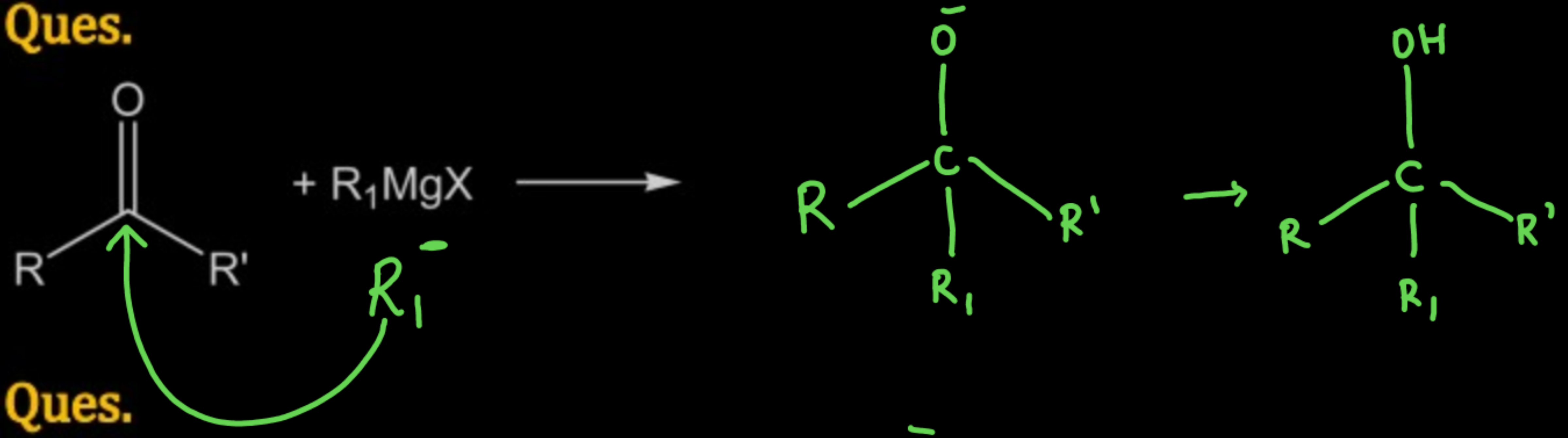
Note: This reaction is used in the purification & separation of aldehyde.

Ques.

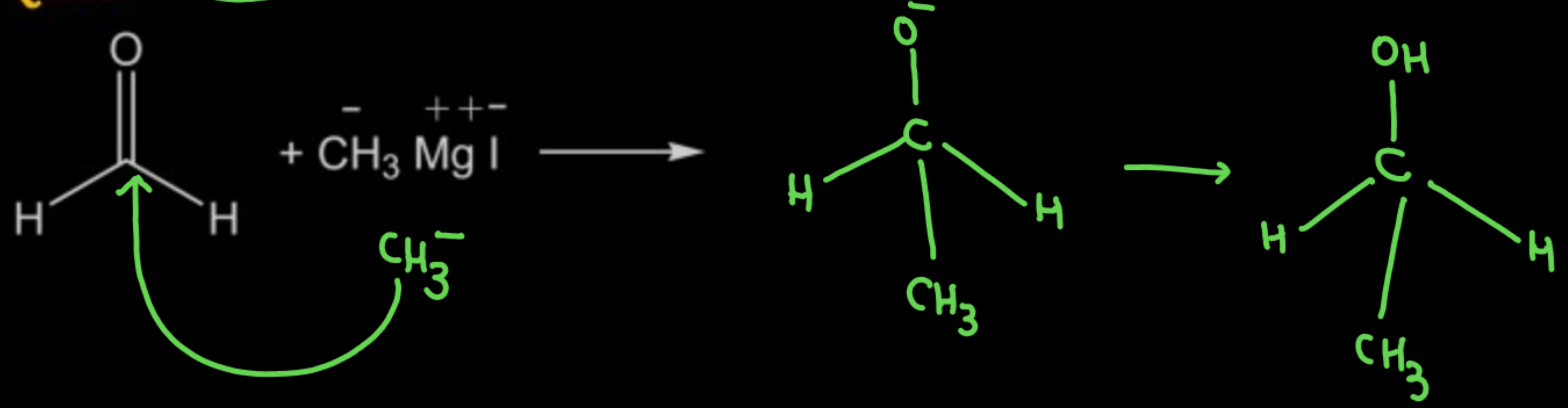


(3) Addition of Grignard reagent ($\overset{-}{R}\overset{2+}{Mg}\overset{-}{X}$)

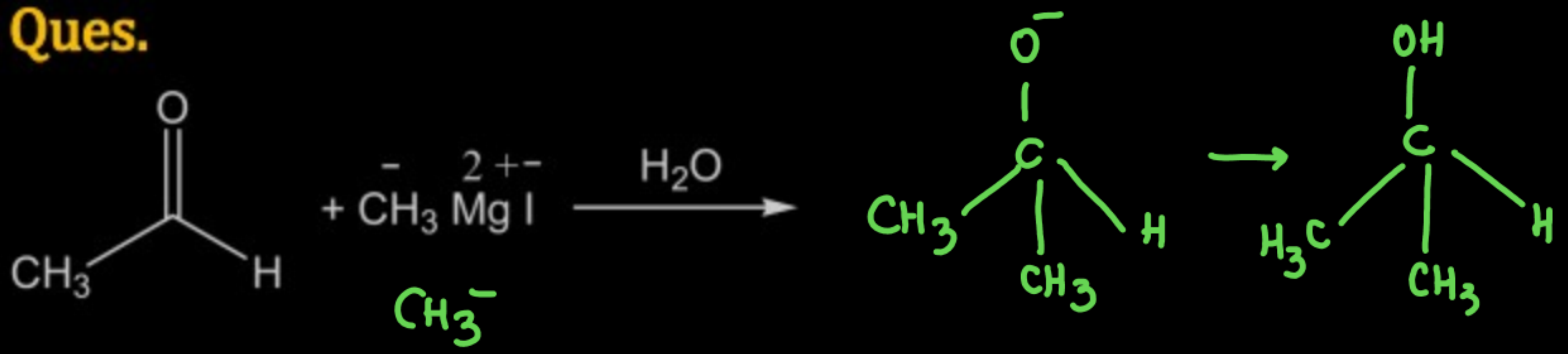
Ques.



Ques.

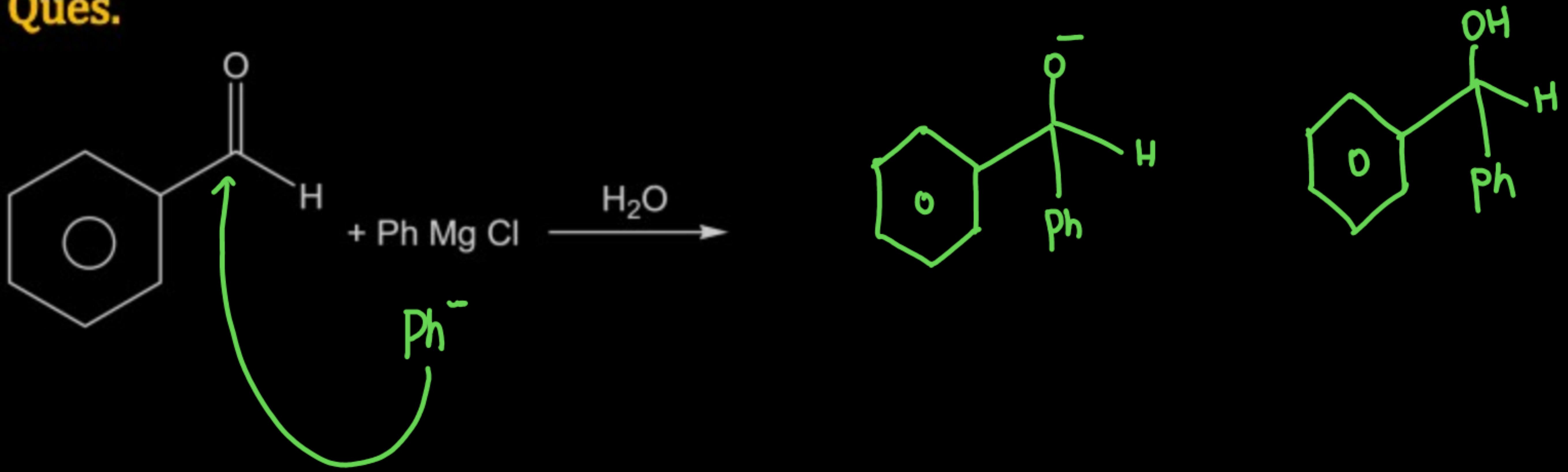


Ques.



O
CH_3
H
- 2+-
+ CH_3 Mg I
CH_3^-
H_2O
O^-
C
CH_3
H
CH_3
OH
C
H_3C
H
CH_3

Ques.

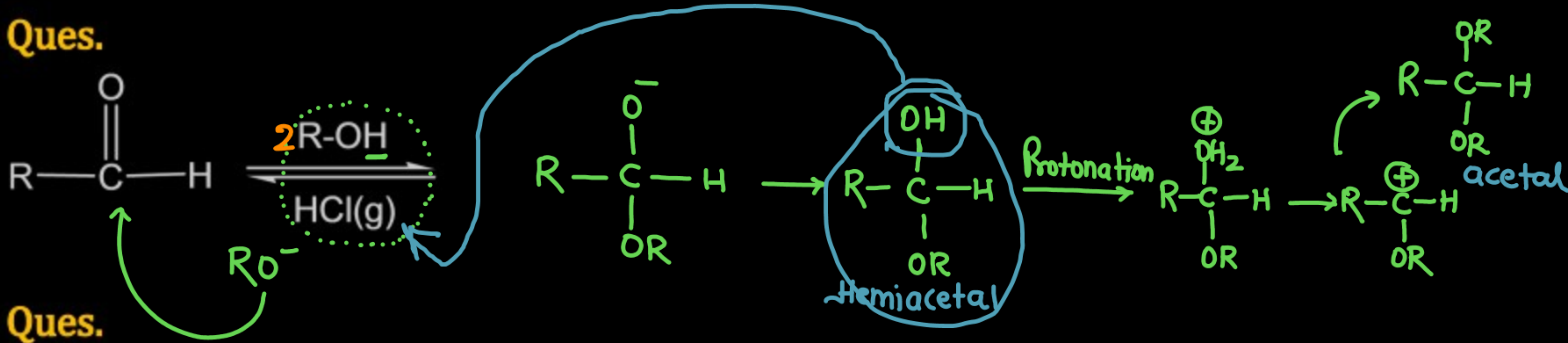


O
H
+ Ph Mg Cl
H_2O
Ph^-
O^-
H
Ph
OH
H
Ph

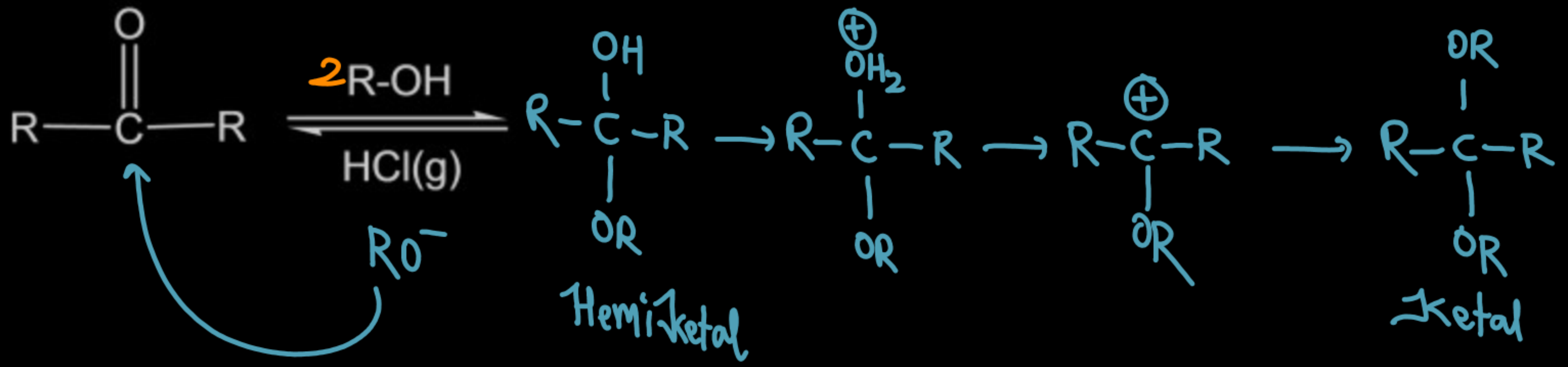
aldehyde → Hemiacetal → acetal
Ketone → Hemiketal → ketal

(4) Addition of R – OH (alcohol)

Ques.



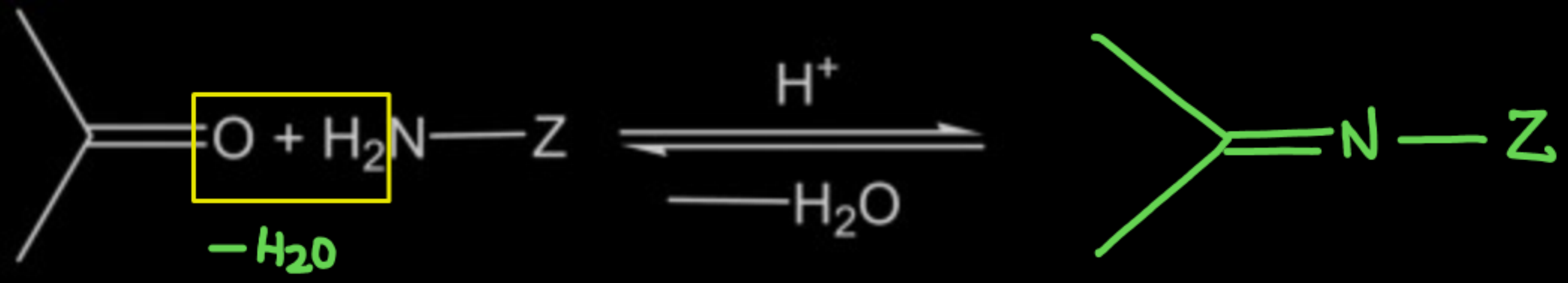
Ques.



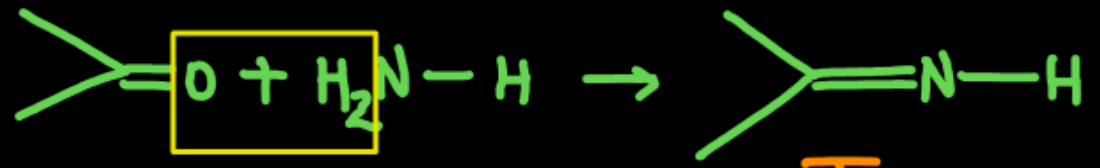
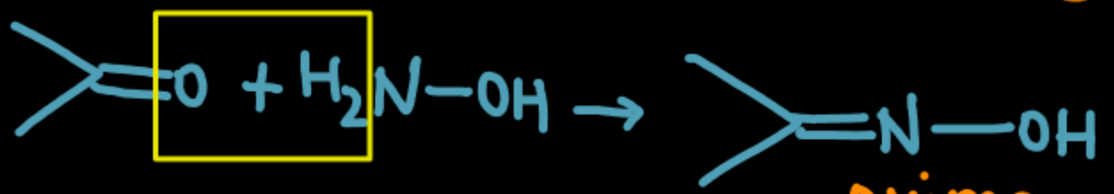
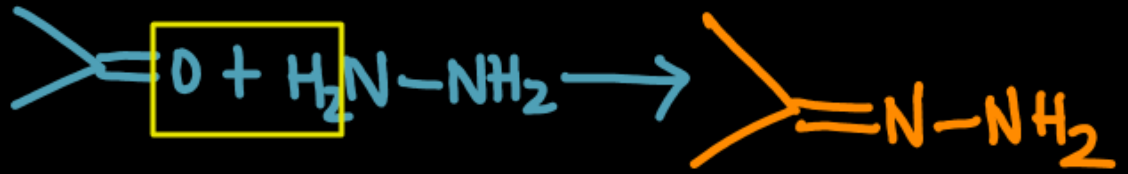
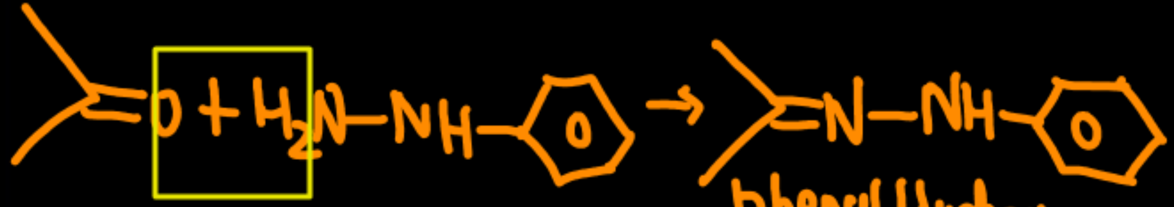
Amine + aldehyde/ketone ⟶ H_2O release

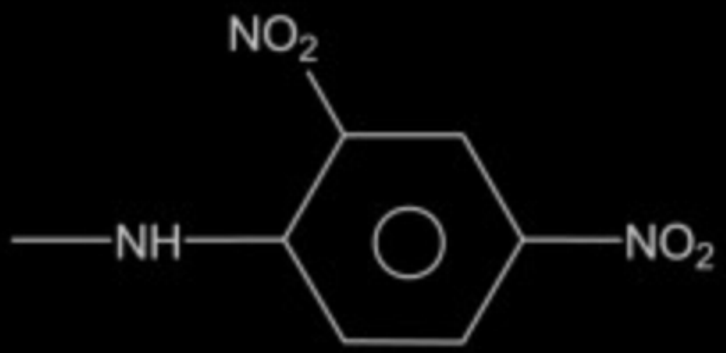
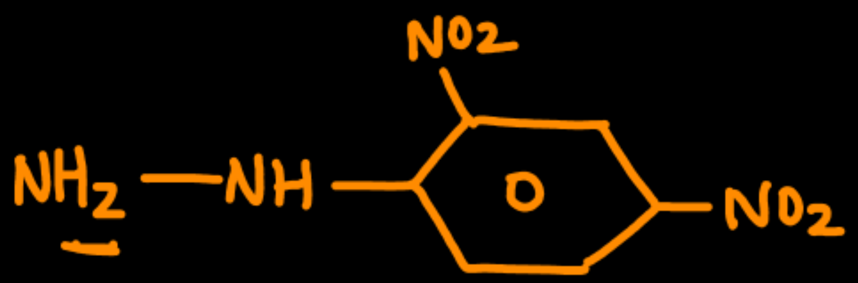
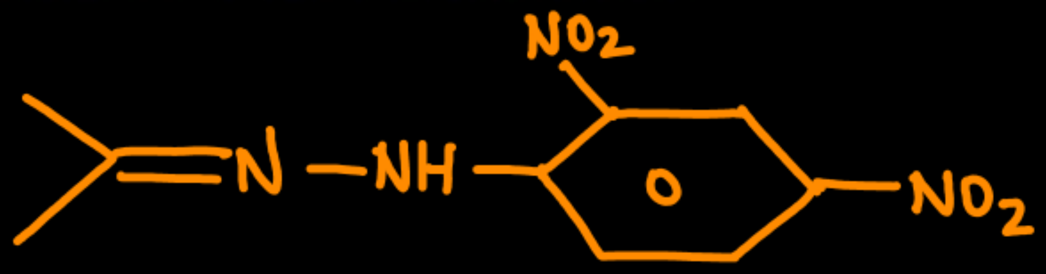
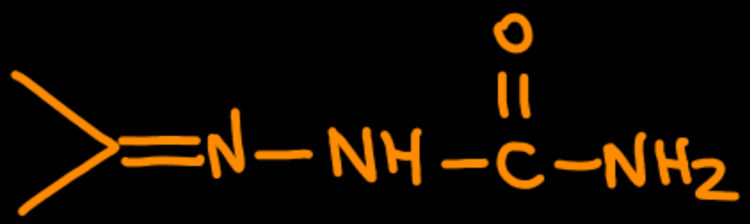
(5) Addition of ammonia and its derevatives

Ques.



Aldehyde or ketone + Amine or Amine derivative $\xrightarrow{-H_2O}$ H_2O release

	Z	Reagent name		Carbonyl derivatives
(1)	$-H$	NH_3	ammonia	 Imine
(2)	$-R$	NH_2-R	amine	 substituted Imine
(3)	$-OH$	NH_2-OH	Hydroxyl amine	 oxime
(4)	$-NH_2$	$\ddot{N}H_2-\ddot{N}H_2$	Hydrazine	 Hydrazone
(5)	$-NH-C_6H_5$	$NH_2-NH-C_6H_5$	Phenyl Hydrazine	 phenyl Hydrazone

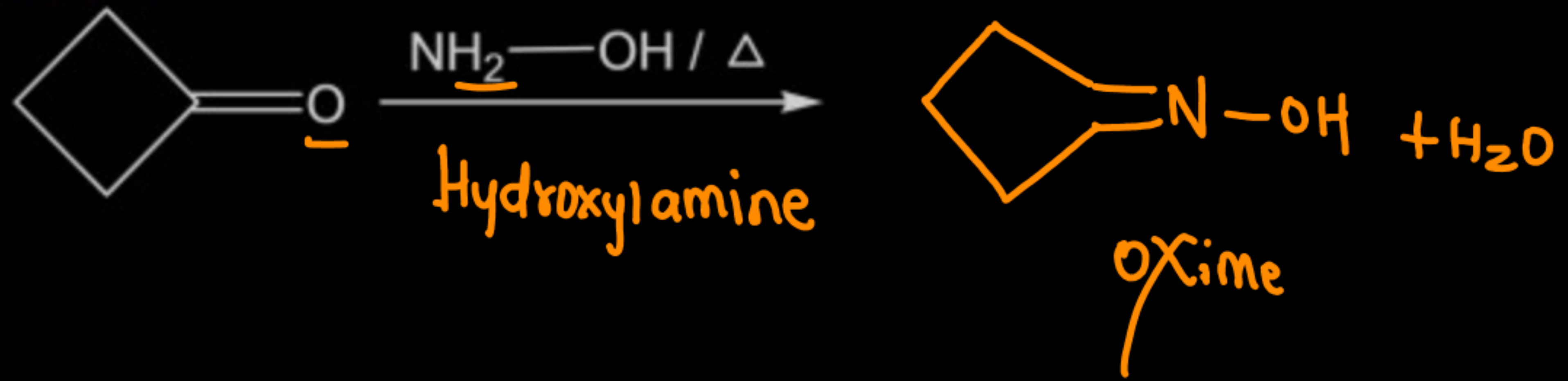
Z	Reagent name	Carbonyl derivatives
(6) 	 2,4-dinitrophenyl Hydrazine	 2,4-dinitrophenyl Hydrazone
(7) $-NH-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$	$NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2$ Semicarbazide	 Semicarbazone

Ques.



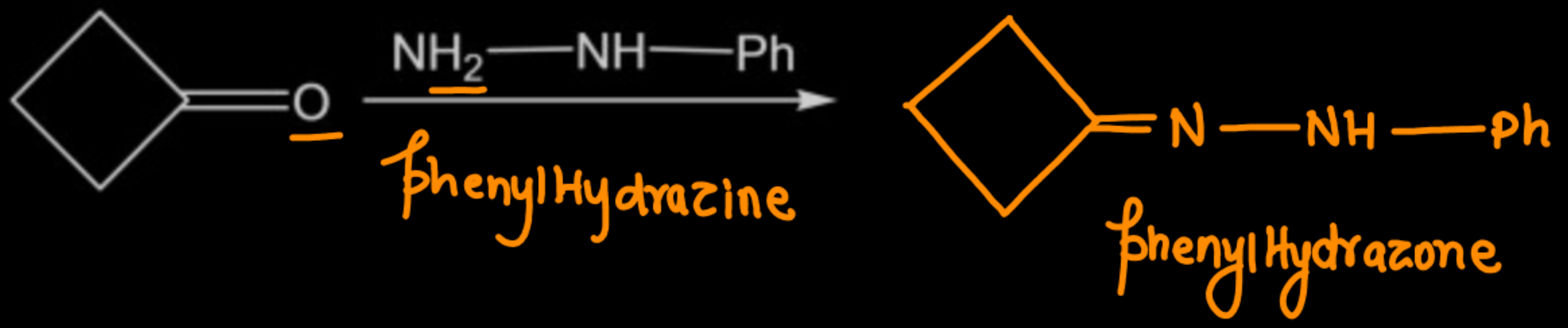
O
NH2—NH2 / Δ
Hydrazine
N—NH2 + H2O
Hydrazone

Ques.



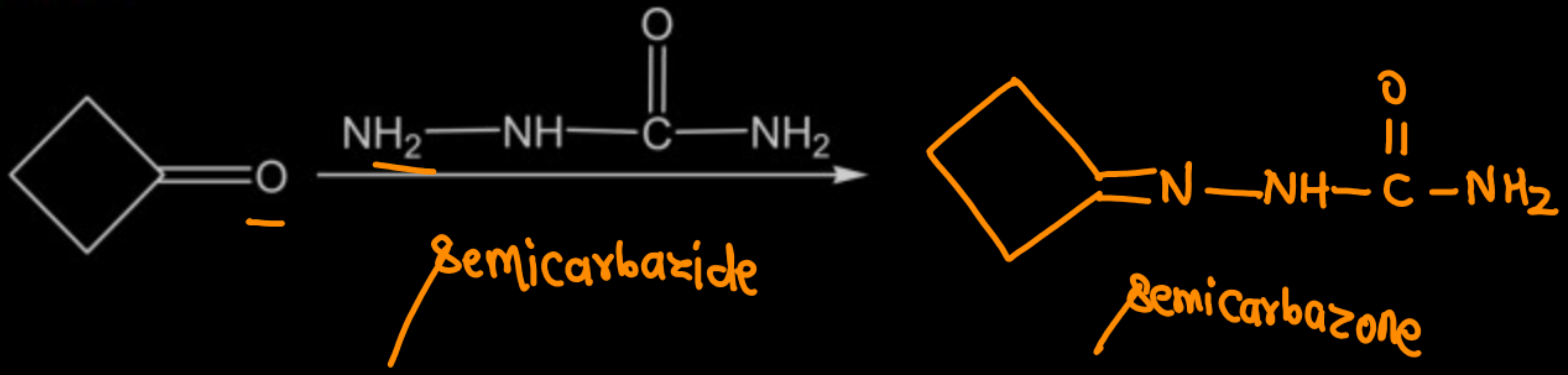
O
NH2—OH / Δ
Hydroxylamine
N-OH +H2O
oxime

Ques.



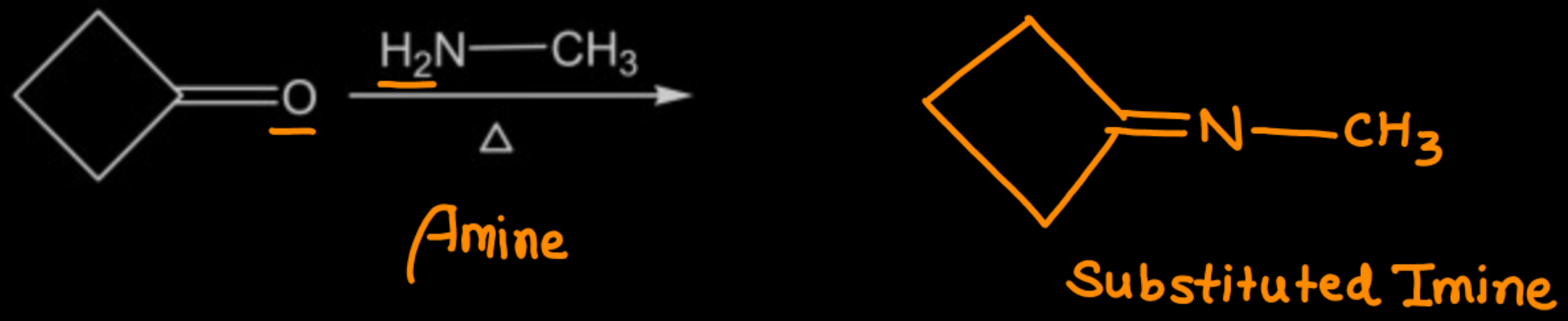
NH2—NH—Ph
Phenyl Hydrazine
N—NH—Ph
Phenyl Hydrazone

Ques.



NH2—NH—C—NH2
Semicarbazide
N—NH—C—NH2
Semicarbazone

Ques.

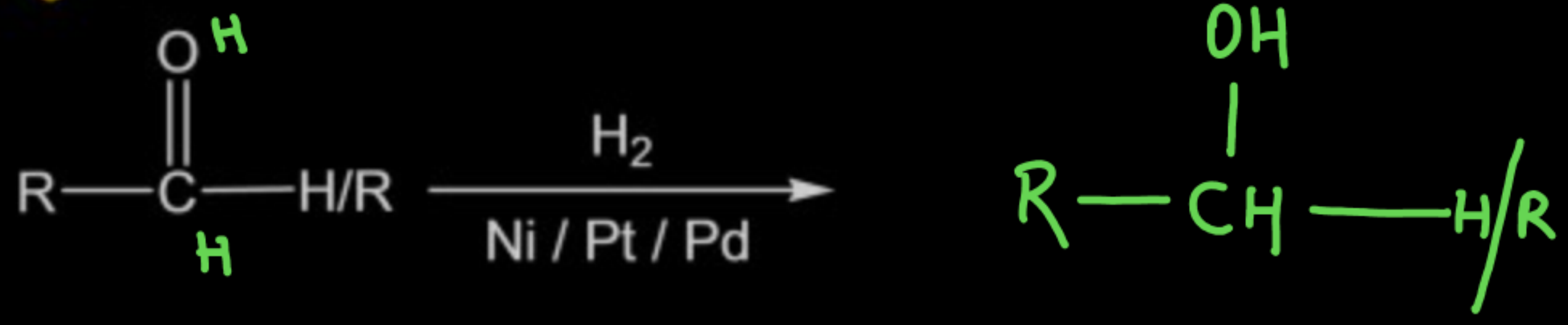


Reduction

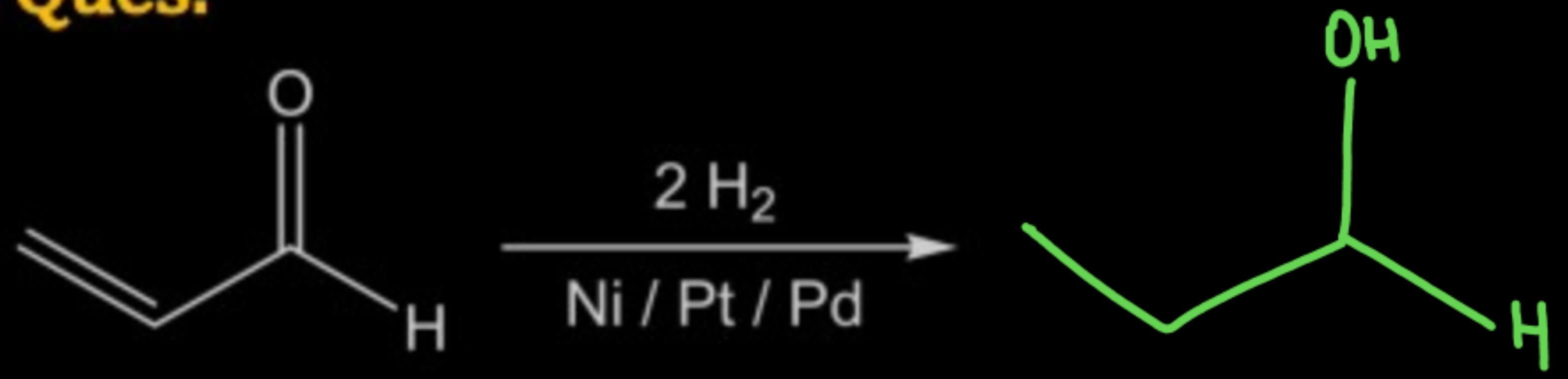
- ✓ (i) Catalytic Hydrogenation $\xrightarrow[Ni/Pt/Pd]{H_2}$
- ✓ (ii) Reducing agent ($LiAlH_4$, $NaBH_4$)
- ✓ (iii) Bouveault Blank Reduction $\xrightarrow[\text{Reduction}]{Na-EtOH}$

(i) Catalyst hydrogenation:

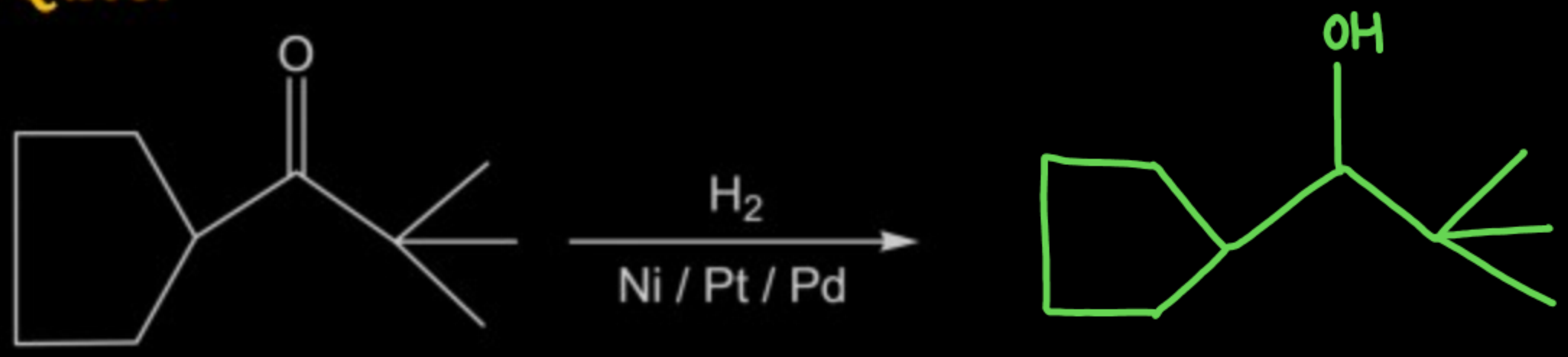
Ques.



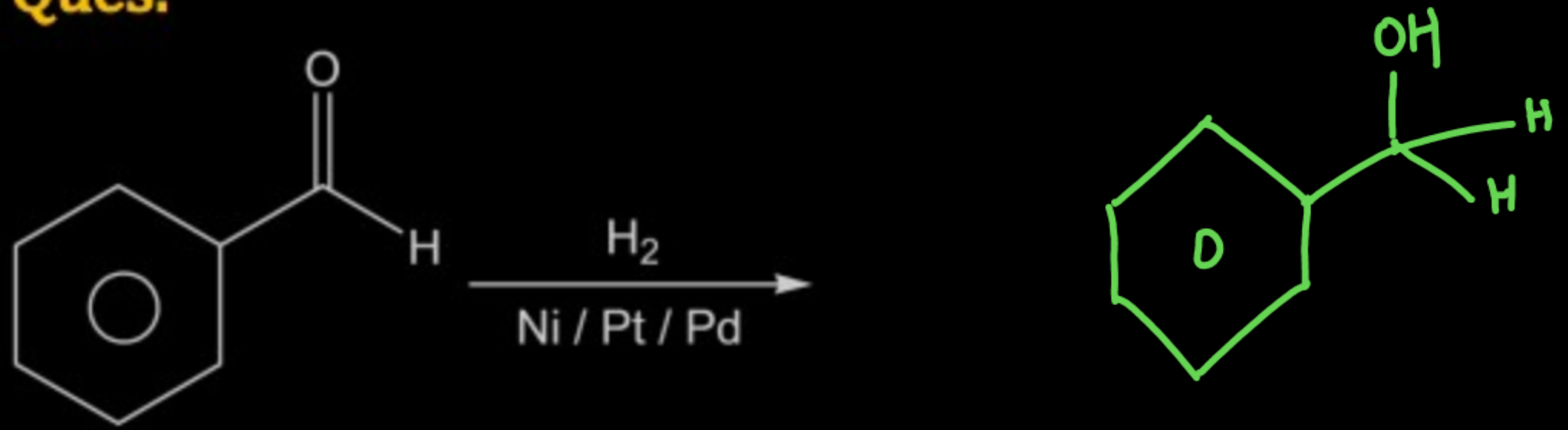
Ques.



Ques.

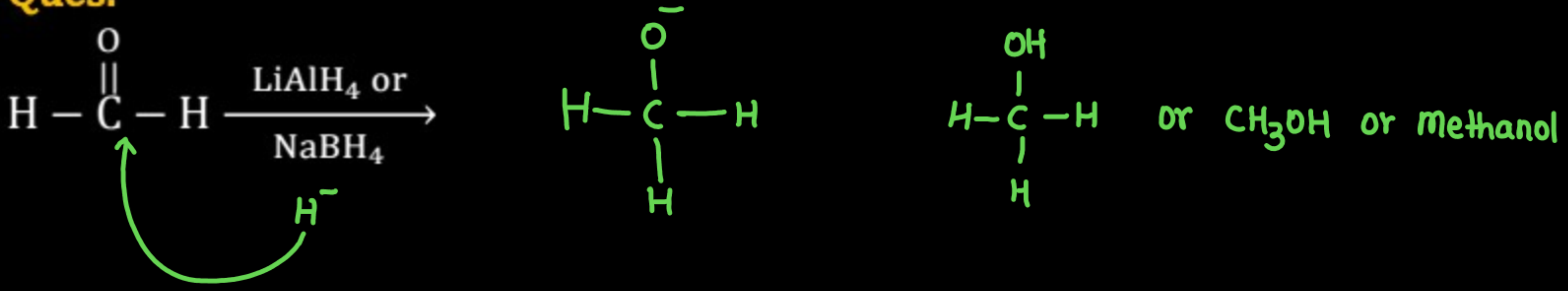


Ques.

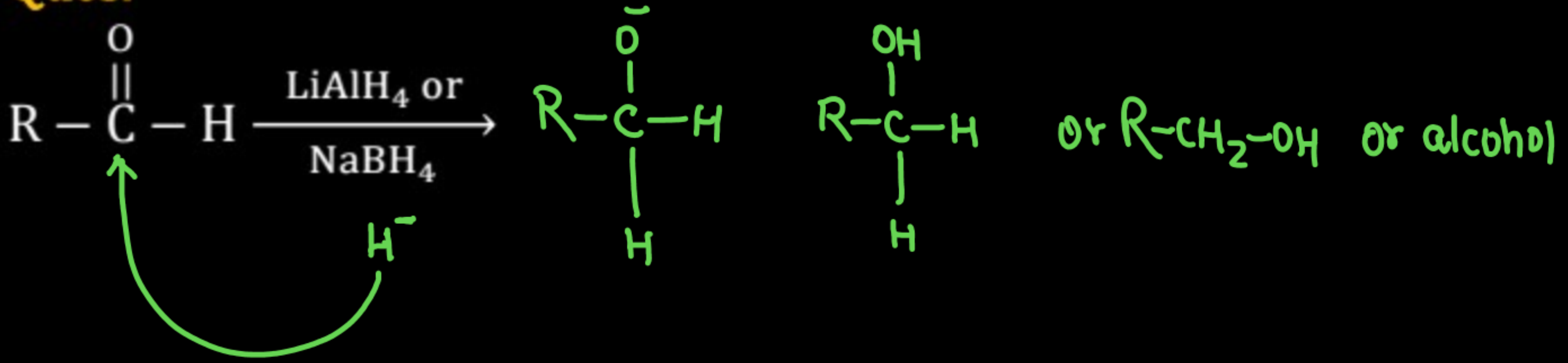


(ii) By $LiAlH_4$ & $NaBH_4$:

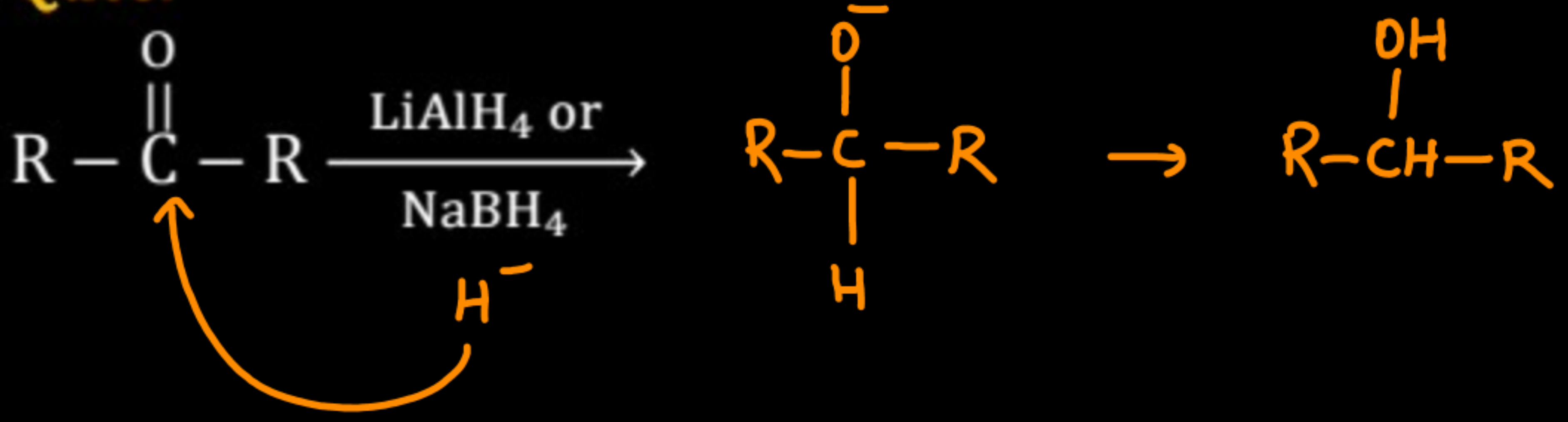
Ques.



Ques.



Ques.



aldehyde $\xrightarrow{\text{Reduce}}$ 1° alcohol

ketone $\xrightarrow{\text{Reduce}}$ 2° alcohol

(iii) Bouveault-Blanc reduction:

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\text{Metal–base}]{\text{Na / EtOH}} R-CH_2-OH$$

(H_2 gas)

aldehyde ⟶ 1° alcohol

ketone ⟶ 2° alcohol

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R' \xrightarrow[\text{NaBH}_4]{\text{LiAlH}_4\text{ or}} 2^\circ \text{ alcohol}$$

$$\xrightarrow{\text{Na-EtOH}} 2^\circ \text{ alcohol}$$

Ques.

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow[\text{HCl}]{\text{Zn–Hg}} R-CH_3$$

Clemmenson
Reduction
Reaction

Ques.

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-R' \xrightarrow[OH^-]{\ddot{N}H_2-\ddot{N}H_2} R-CH_2-R'$$

Wolf Kishner
Reduction

Reduction of Hydrocarbon: -

(i) Clemenson reduction:

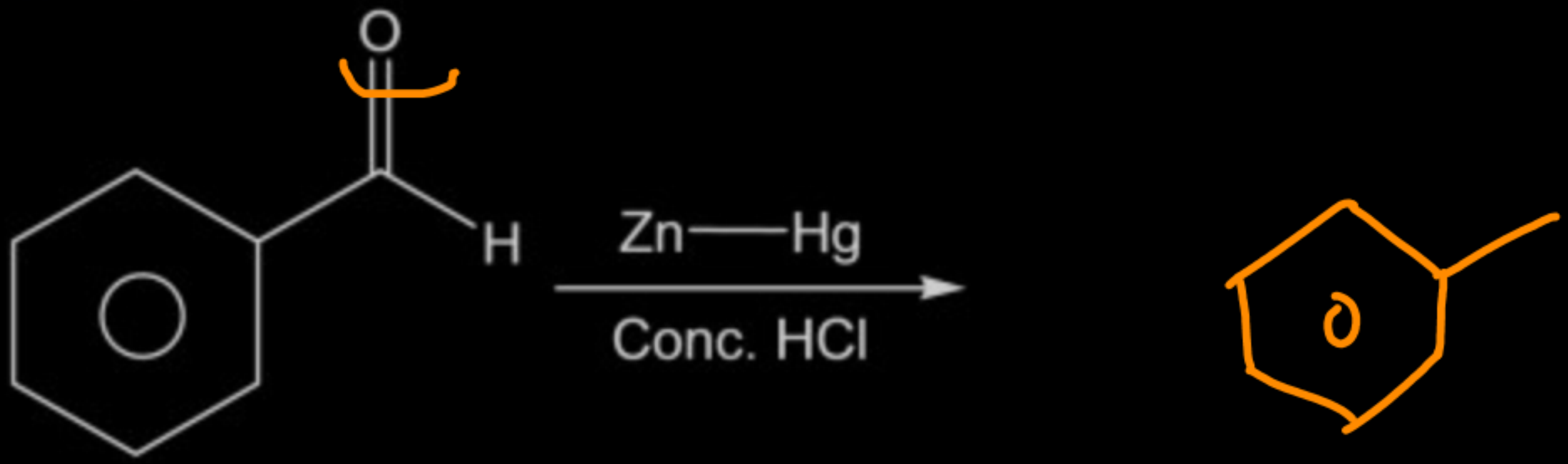
Ques.

$$R-\overset{\overset{O}{\parallel}}{C}-H \xrightarrow[\text{(Conc.HCl)}]{\text{Zn-Hg}} R-CH_3$$

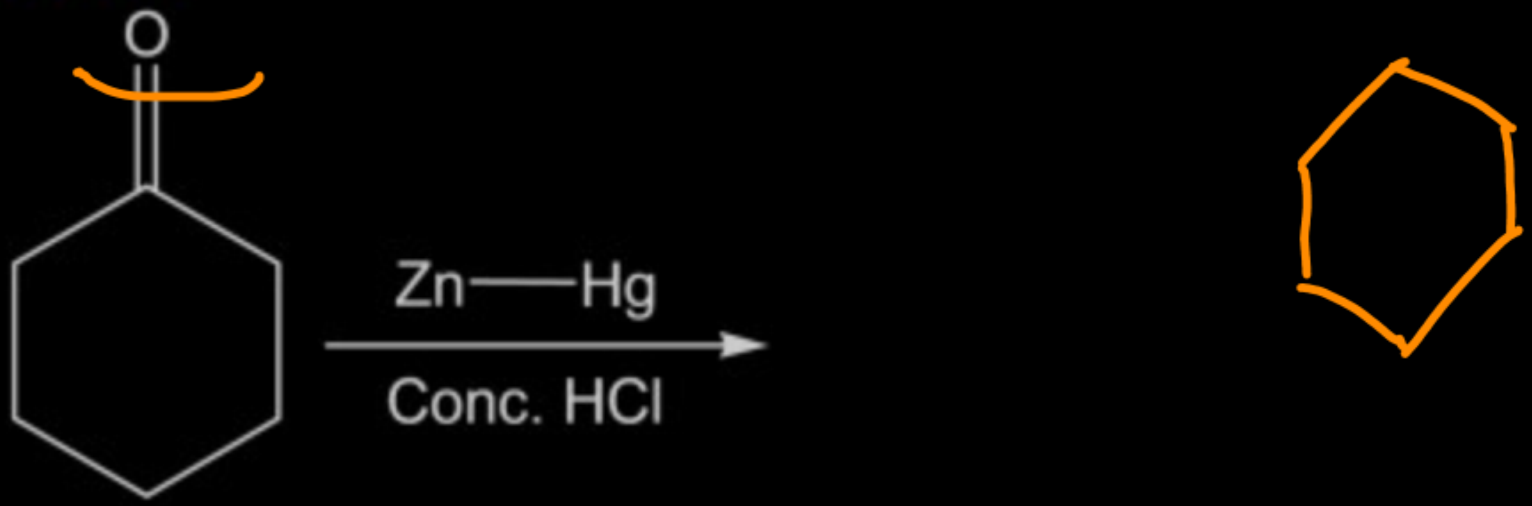
Ques.

$$R-\overset{\overset{O}{\parallel}}{C}-R \xrightarrow[\text{(Conc.HCl)}]{\text{Zn-Hg}} R-CH_2-R$$

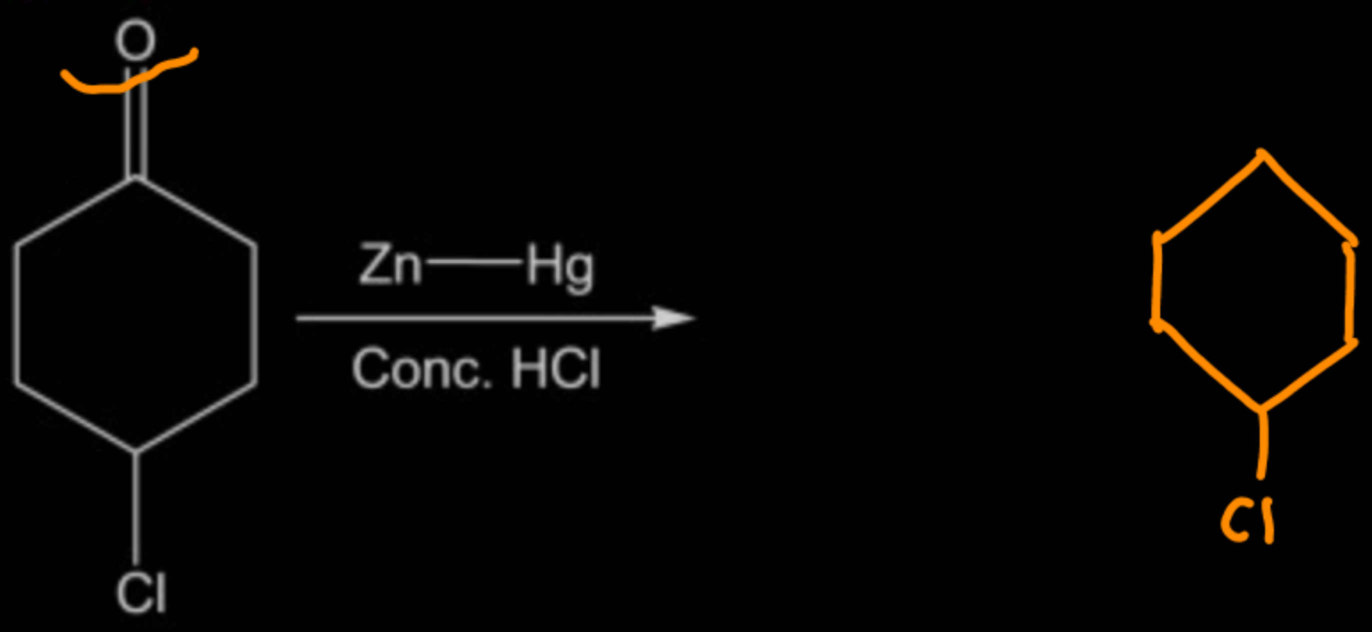
Ques.



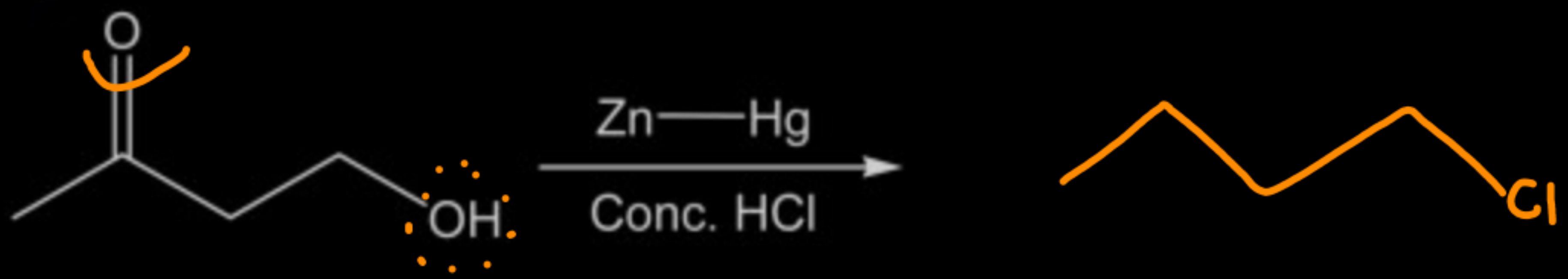
Ques.



Ques.

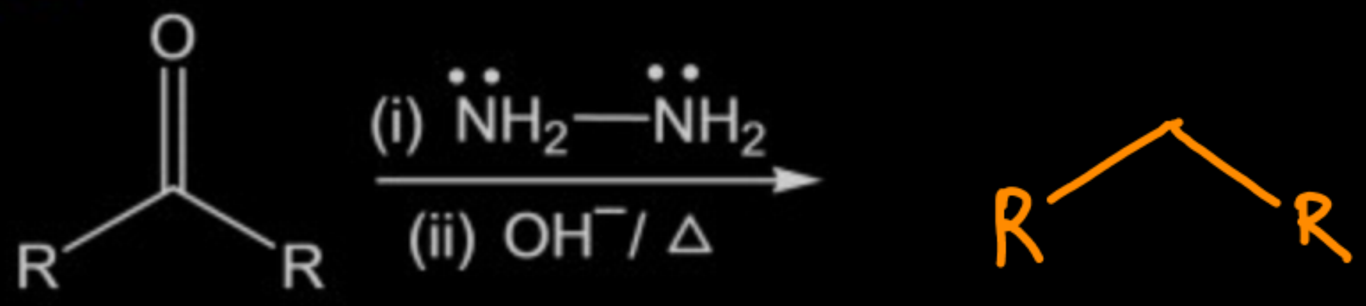


Ques.

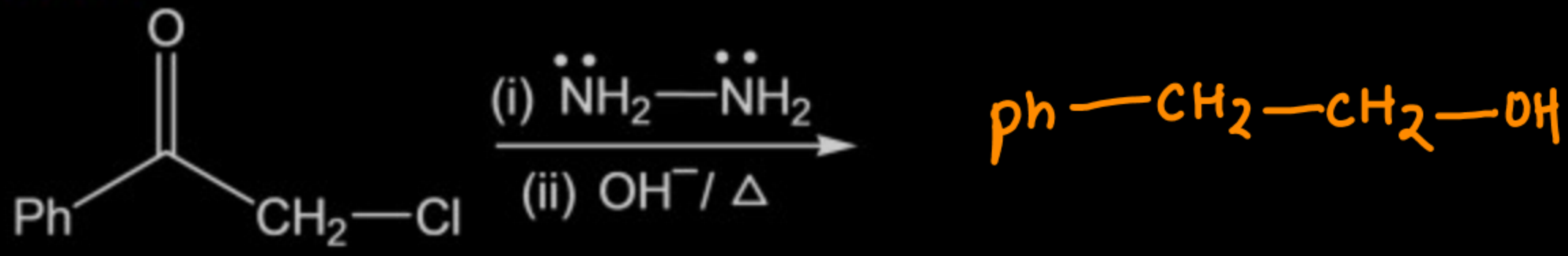


(ii) Wolf-Kishner's reduction:

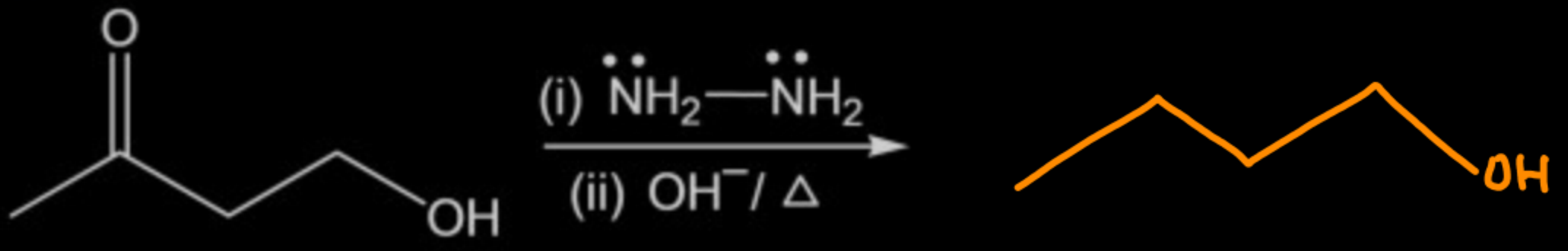
Ques.



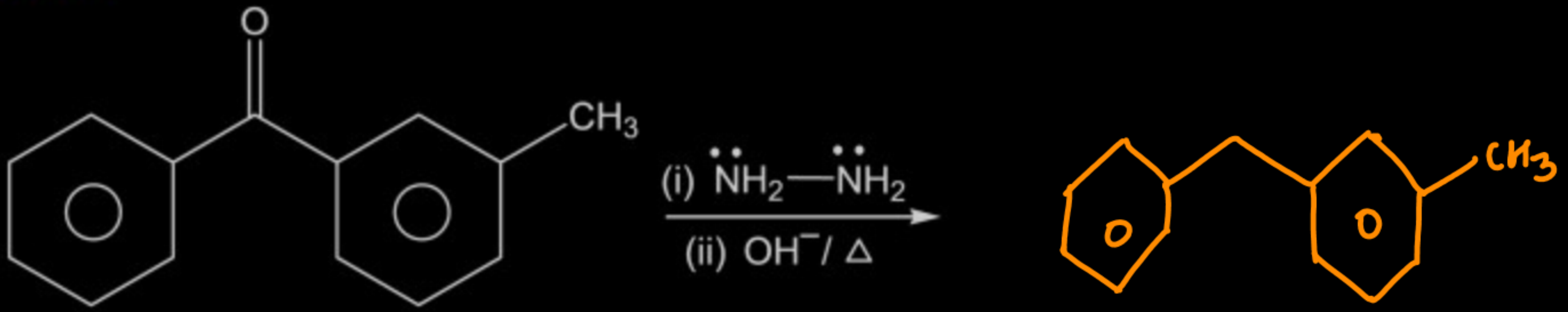
Ques.



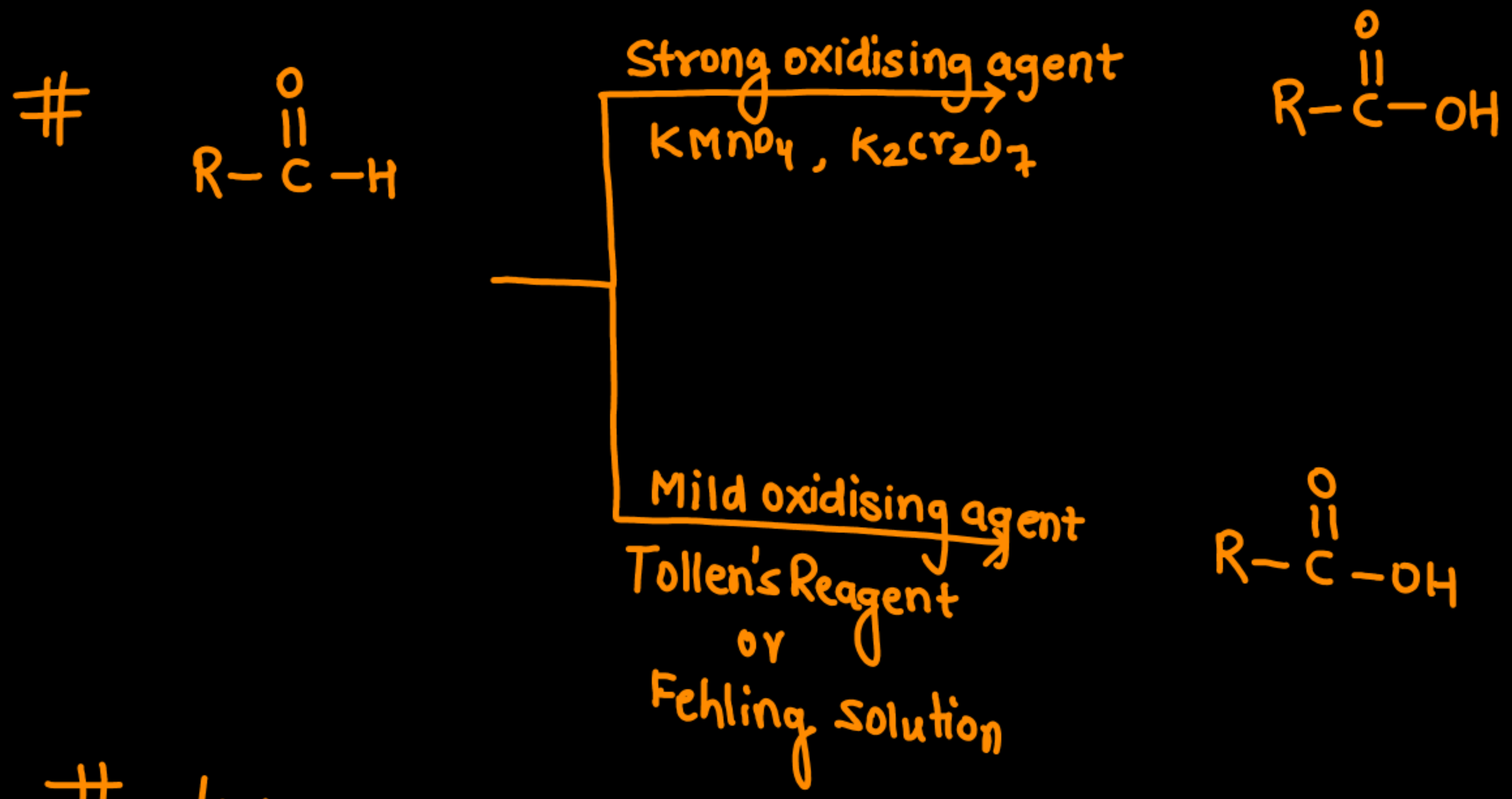
Ques.



Ques.



Oxidation of Aldehyde/Ketone



Ketone donot oxidise further.

Oxidation of Aldehyde & Ketone:

Ques.

$$H-\overset{\overset{O}{\|}}{C}-H \xrightarrow[K_2Cr_2O_7/H^+]{KMnO_4\,/\,H^+\text{ or}} HO-\overset{\overset{O}{\|}}{C}-OH \rightleftharpoons H_2O + CO_2$$

Carbonic acid

Ques.

$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow[K_2Cr_2O_7/H^+]{KMnO_4\,/\,H^+\text{ or}} R-\overset{\overset{O}{\|}}{C}-OH$$

Ques.

$$R-\overset{\overset{\large O}{\|}}{C}-R \xrightarrow[K_2Cr_2O_7/H^+]{KMnO_4\,/\,H^+ \text{ or}}$$

Oxidation of Methyl Ketone

By Haloform Reaction

CHX_3 Haloform

$CHCl_3$ Chloroform

$CHBr_3$ Bromoform

CHI_3 Iodoform (yellow)

Condition: methyl ketone must be present for haloform rxn.

$\left(\overset{O}{\overset{\|}{C}}-CH_3\right)$ group must be present for haloform reaction.

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$, $Ph-\overset{O}{\overset{\|}{C}}-CH_3$, $H-\overset{O}{\overset{\|}{C}}-CH_3$, $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-Ph$

Examples:

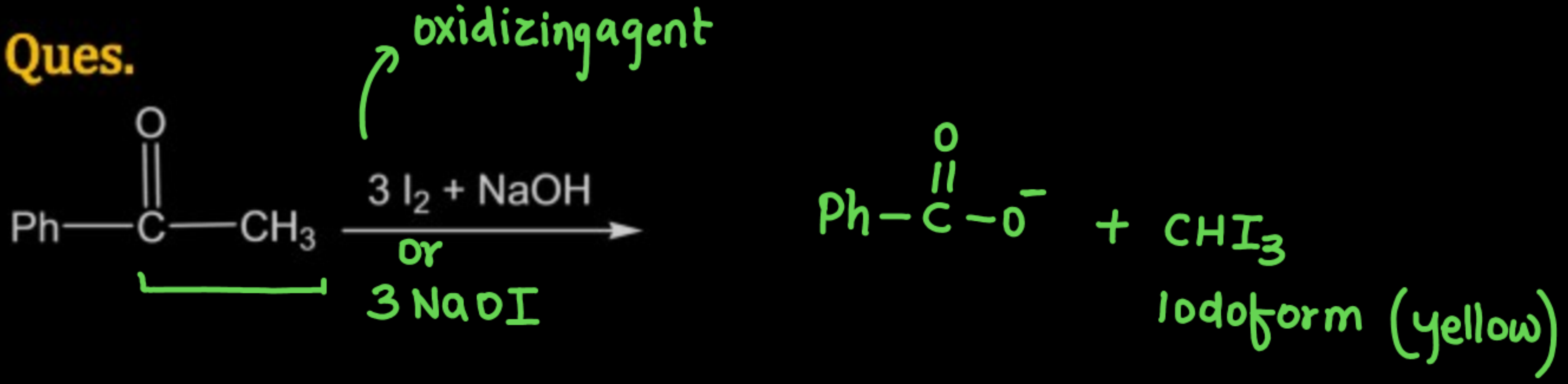
(1) $CH_3-\overset{\overset{O}{\|}}{C}-H$

(2) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(3) $CH_3-\overset{\overset{O}{\|}}{C}-Ph$

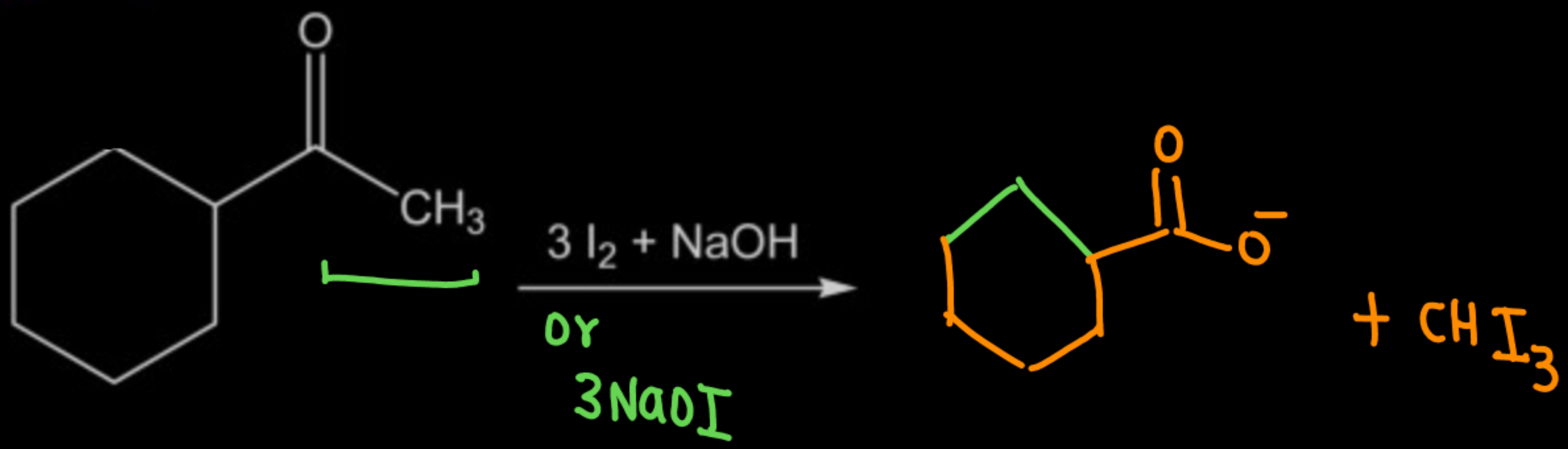
(1) $CH_3-\overset{\overset{O}{\|}}{C}-R$

Ques.



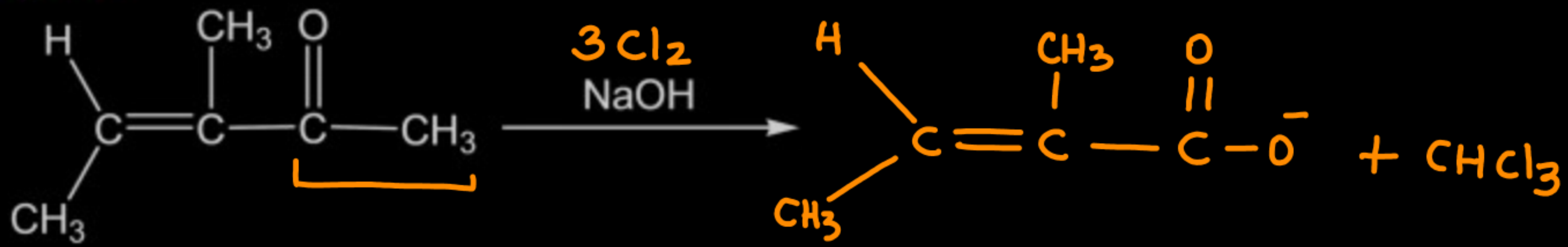
oxidizingagent
O
Ph—C—CH3
3 I2 + NaOH
or
3 NaOI
O
Ph–C–O⁻
+ CHI3
Iodoform (yellow)

Ques.

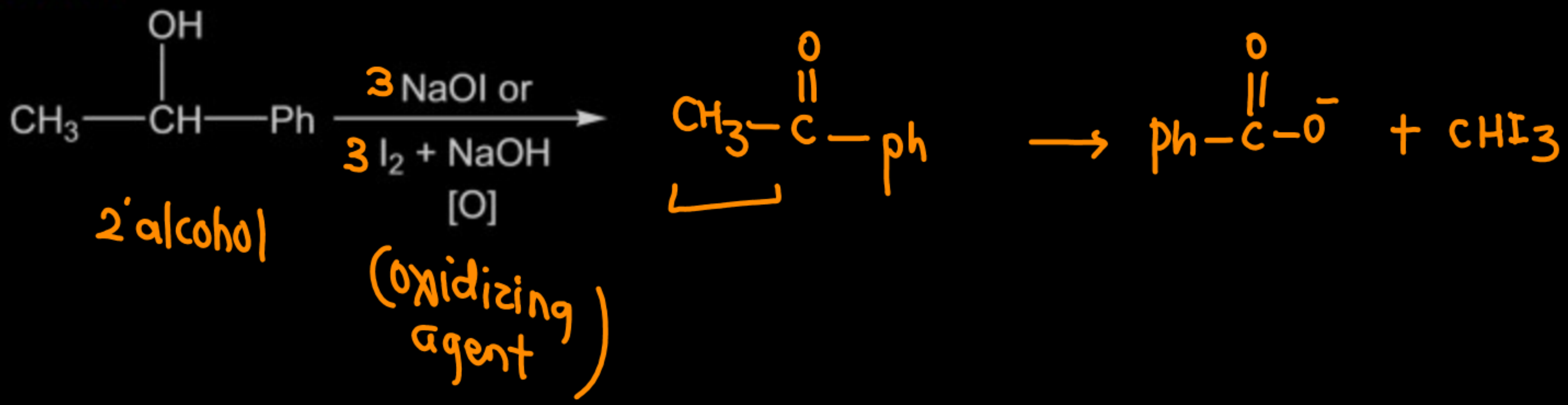


O
CH3
3 I2 + NaOH
or
3NaOI
O
O⁻
+ CHI3

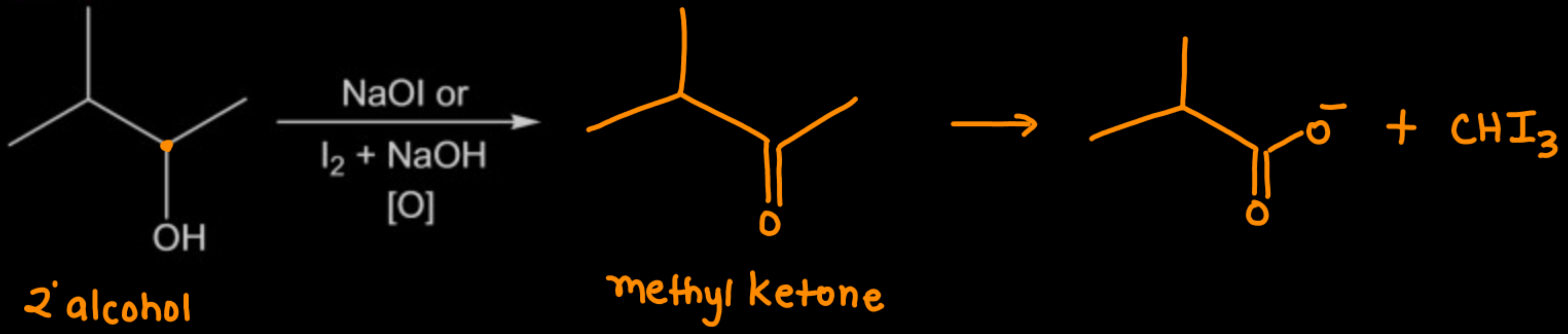
Ques.


3 Cl2
NaOH
+ CHCl3

Ques.

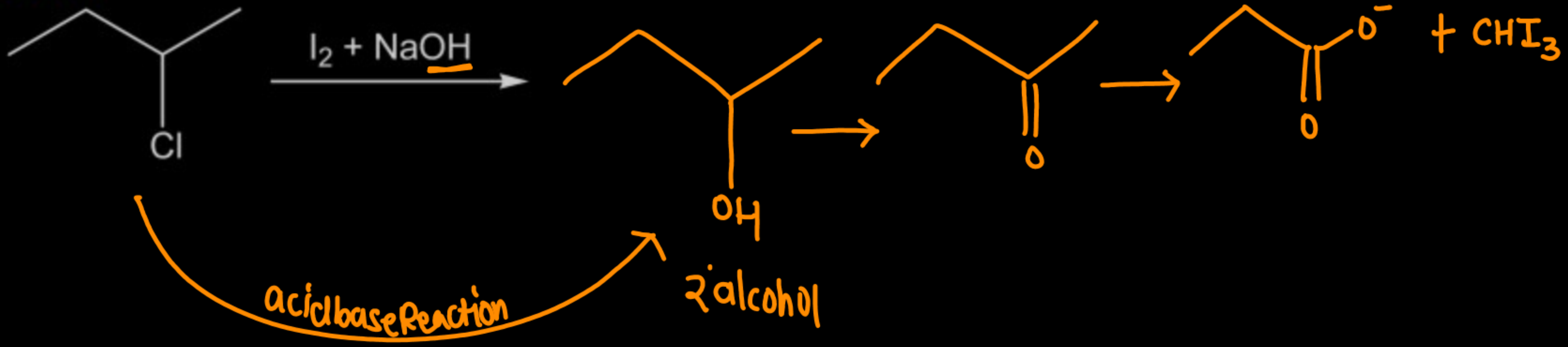

3 NaOI or
3 I2 + NaOH
[O]
2' alcohol
(oxidizing agent)
+ CHI3

Ques.



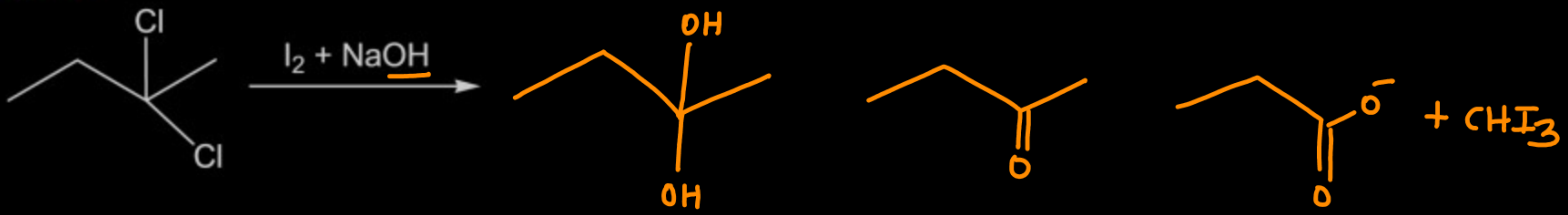
NaOI or
I2 + NaOH
[O]
OH
2° alcohol
methyl ketone
O
O⁻
+ CHI3

Ques.

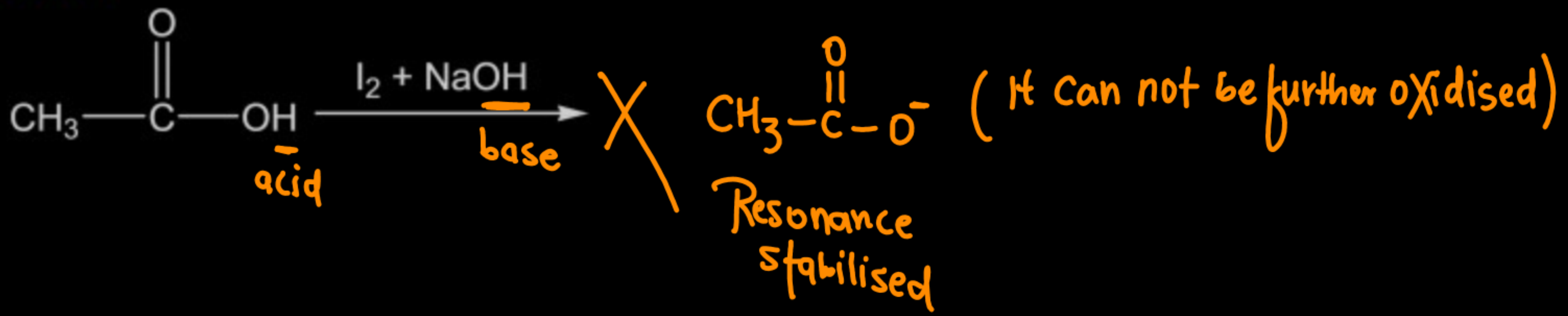


I2 + NaOH
Cl
acid base Reaction
OH
2° alcohol
O
O⁻
+ CHI3

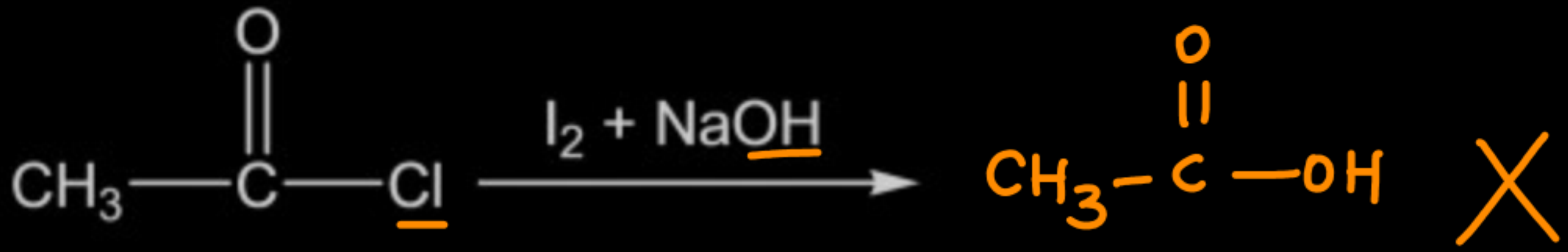
Ques.


Cl
Cl
I2 + NaOH
OH
OH
O
O
O
+ CHI3

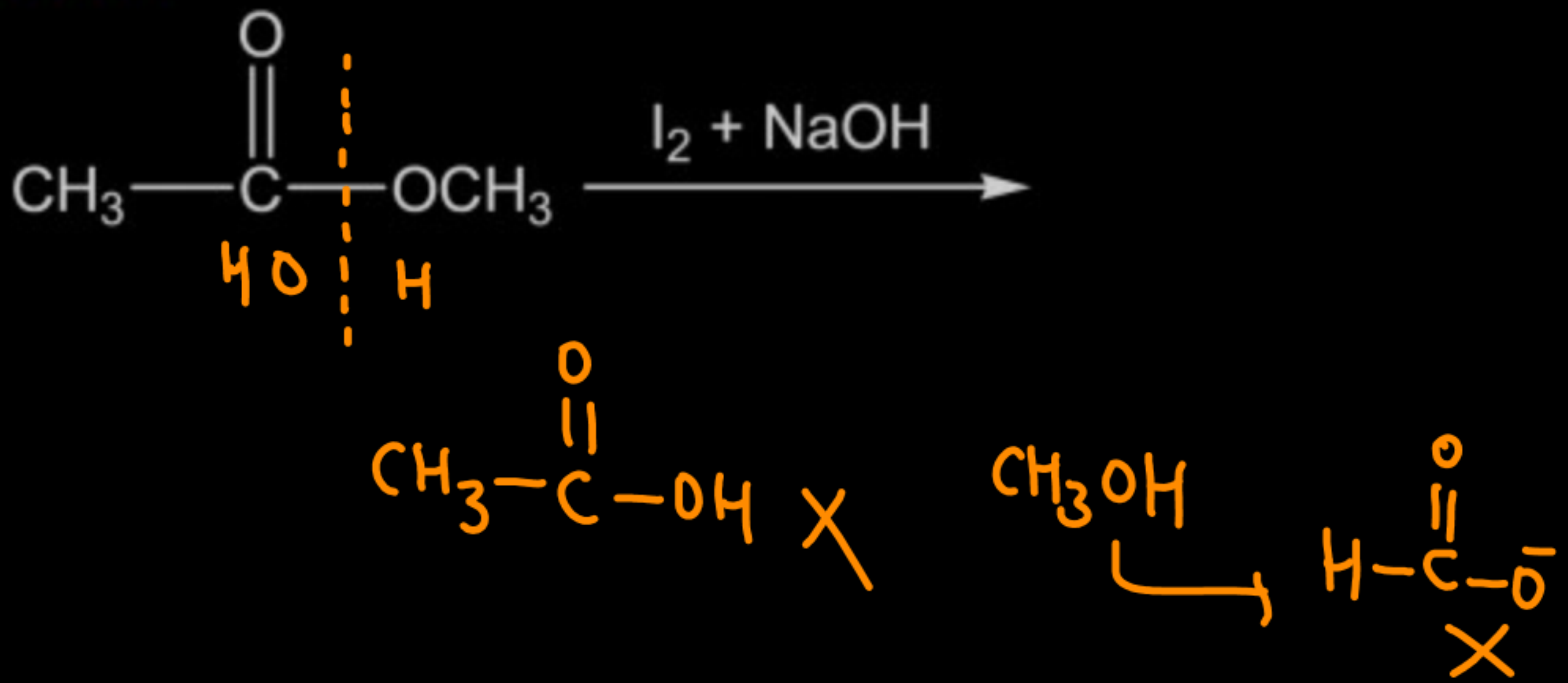
Ques.


O
CH3—C—OH
acid
I2 + NaOH
base
O
CH3–C–O
(It can not be further oxidised)
Resonance stabilised

Ques.

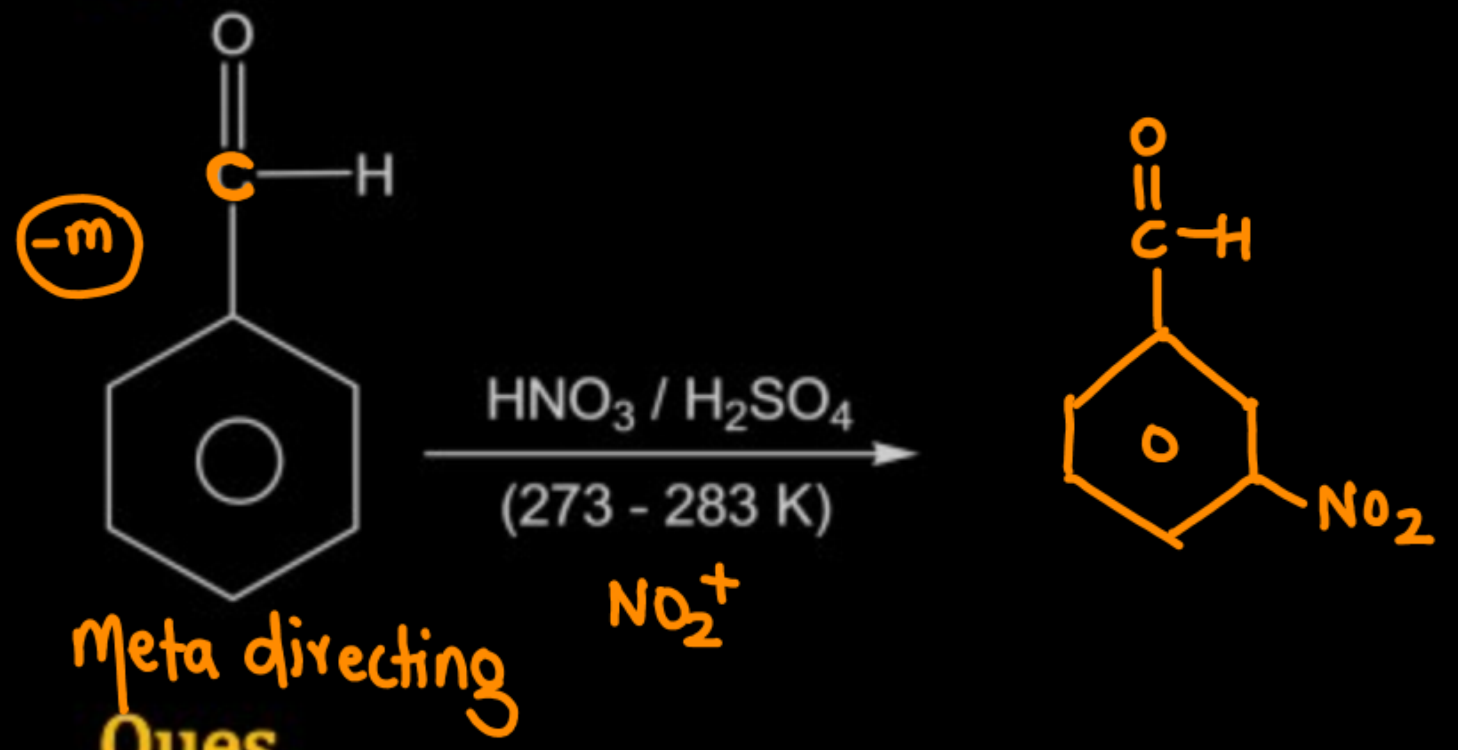

CH3—C(=O)—Cl
I2 + NaOH
CH3—C(=O)—OH

Ques.


CH3—C(=O)—OCH3
I2 + NaOH
HO
H
CH3—C(=O)—OH
CH3OH
H—C(=O)—O⁻

Nitration:

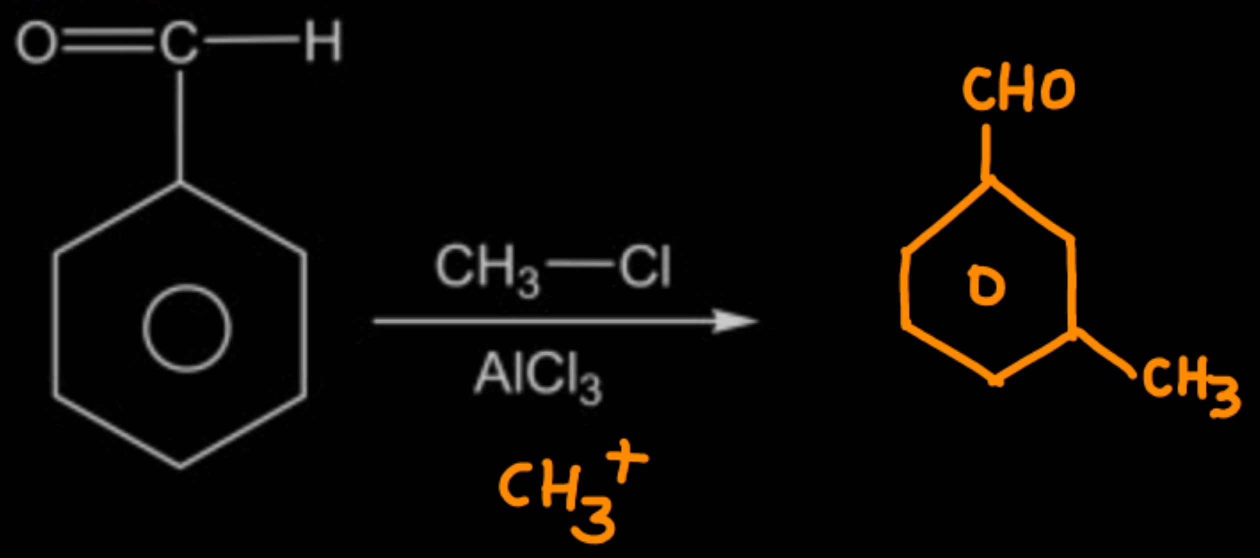
Ques.



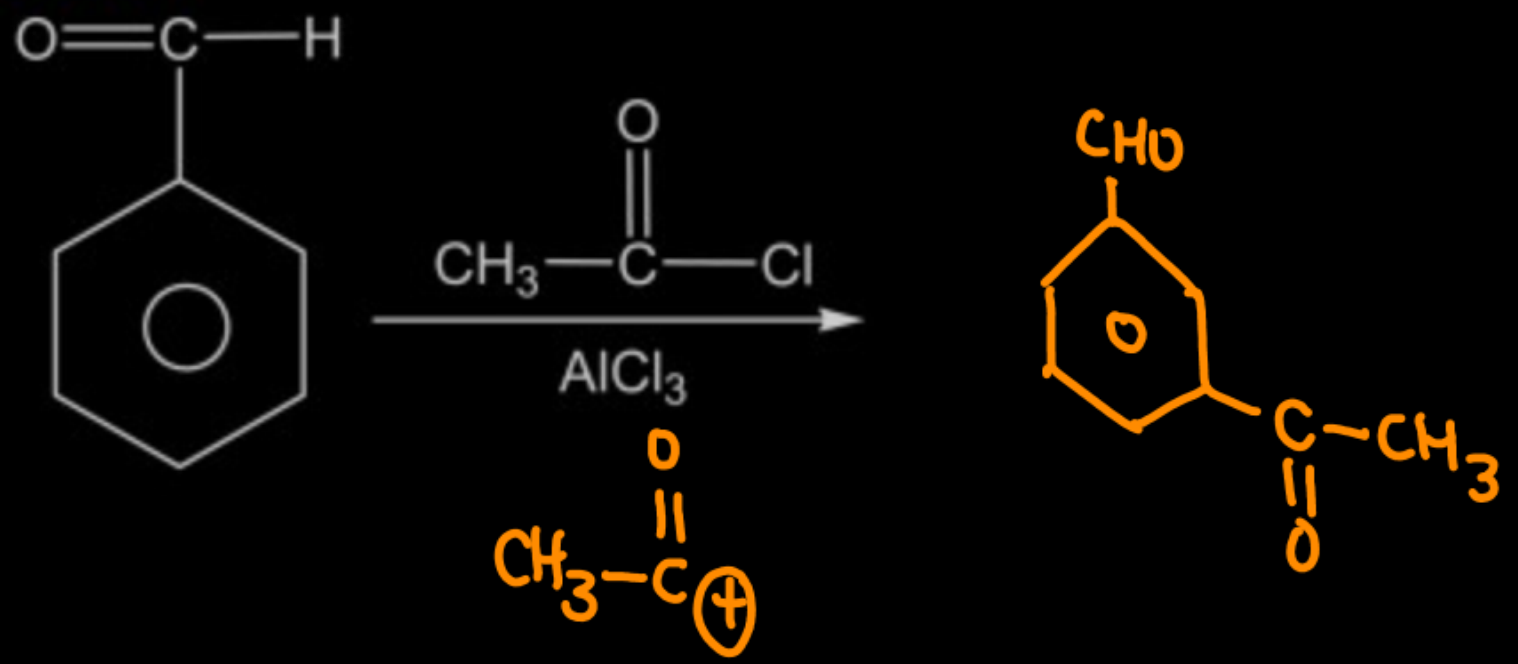
Ques.



Ques.

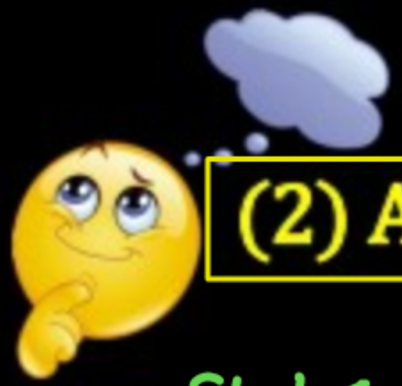

O=C—H
CH3—Cl
AlCl3
CH3+
CHO
CH3

Ques.


O=C—H
CH3—C(=O)—Cl
AlCl3
CH3—C(=O)+
CHO
C—CH3
O

Reaction of Aldehyde & Ketone Related to α-H

1. Aldol Condensatation Reaction → Carbonyl must have α H & dil base
2. Cannizaro Reaction → Carbonyl do have α H & conc base
3. Test of Aldehyde & ketone.



(2) Aldol Reaction:

- Aldehyde must have "α-H" & dil base

Step 1

$$CH_3-\overset{O}{\overset{\|}{C}}-H \underset{}{\xrightleftharpoons{\text{dil NaOH}}} {}^{\ominus}CH_2-\overset{O}{\overset{\|}{C}}-H$$

(CH_3: acidic H)

Step 2

$$CH_3-\overset{O}{\overset{\|}{C}}-H + \overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_3-\overset{O^-}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\underset{\beta}{\overset{OH}{\overset{|}{C}H}}-\underset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-H$$

original molecule — anion

β-Hydroxy carbonyl (Aldol)

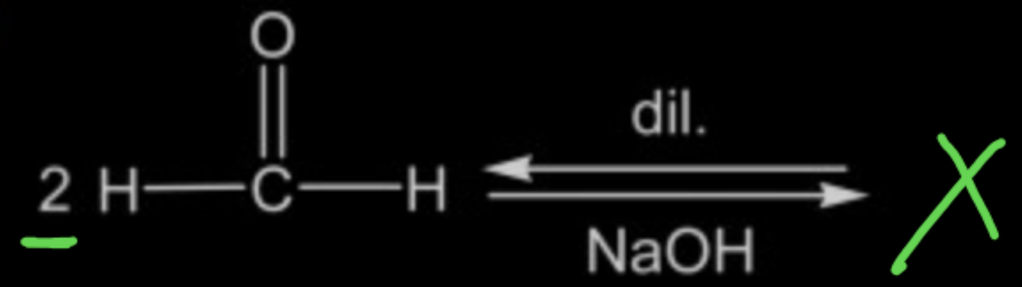
$$\downarrow \Delta, -H_2O$$

$$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H$$

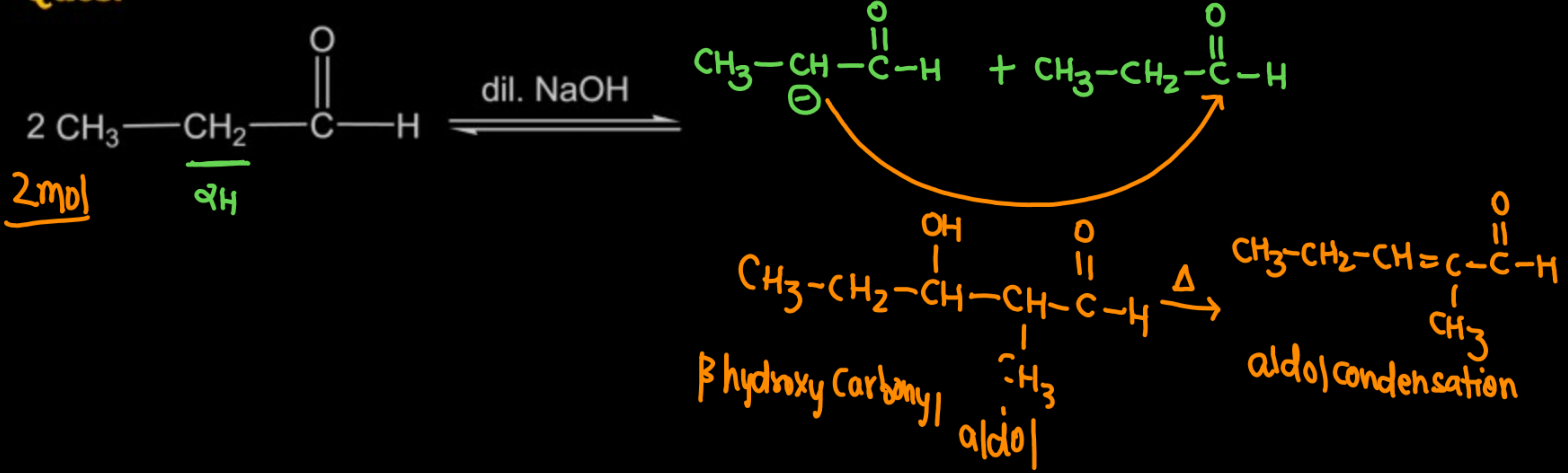
aldol condensation Rxn



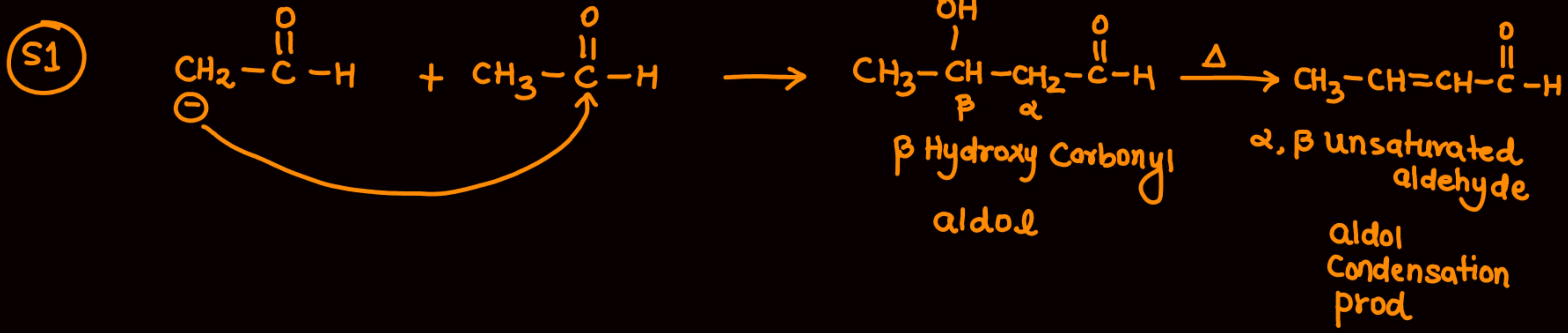
Ques.


2 H—C—H
dil.
NaOH

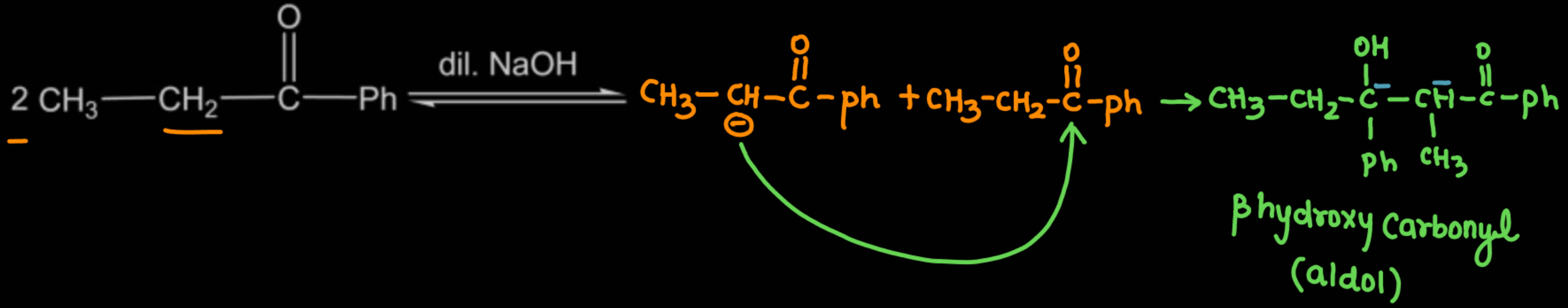
Ques.


2 CH3—CH2—C—H
dil. NaOH
2mol
αH
Δ
β hydroxy Carbonyl
aldol
aldol condensation

$$2\,CH_3-\overset{O}{\overset{\|}{C}}-H \xrightleftharpoons{\text{dil NaOH}}$$

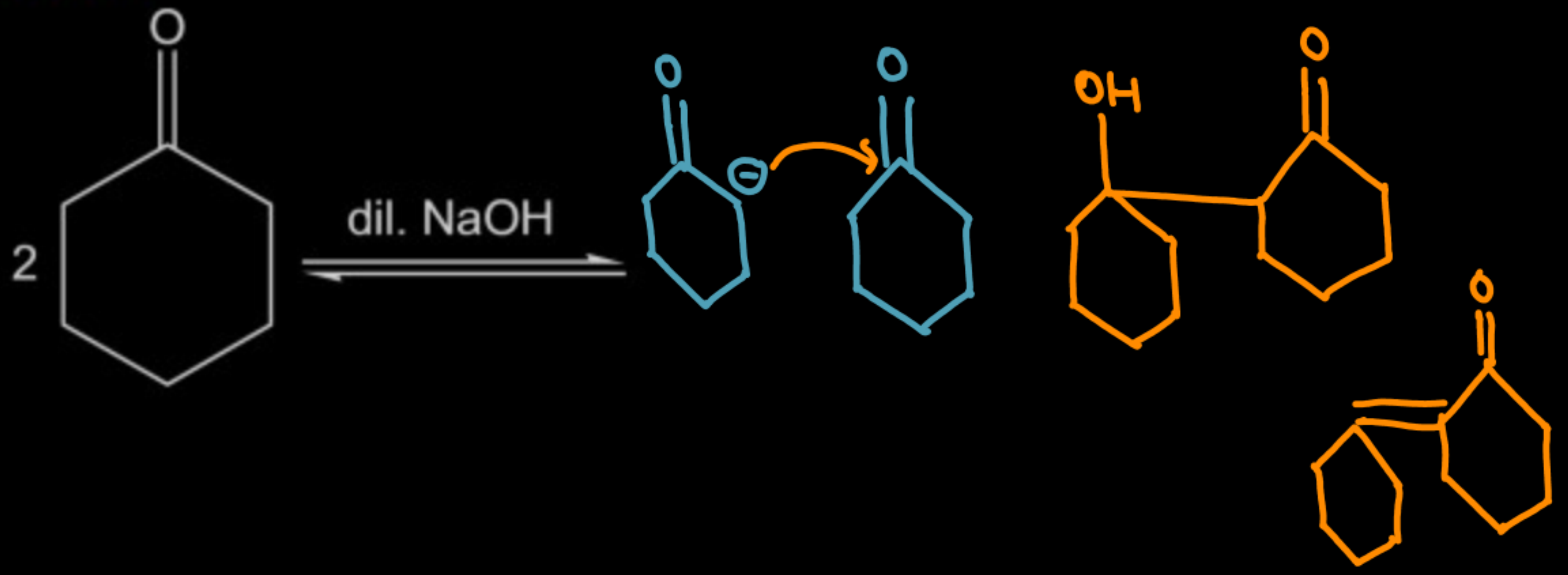


Ques.

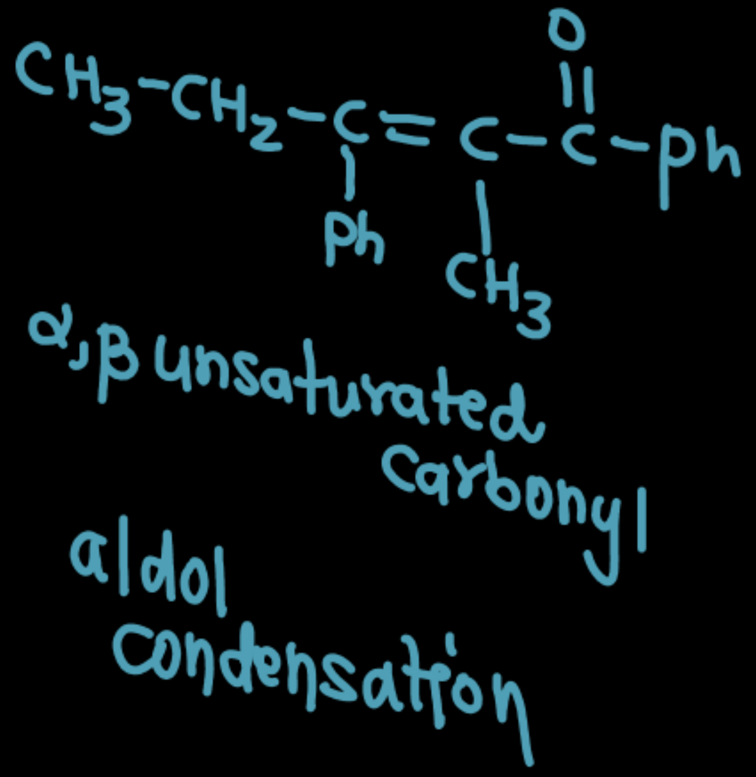


dil. NaOH
β hydroxy carbonyl
(aldol)

Ques.



2
dil. NaOH
OH

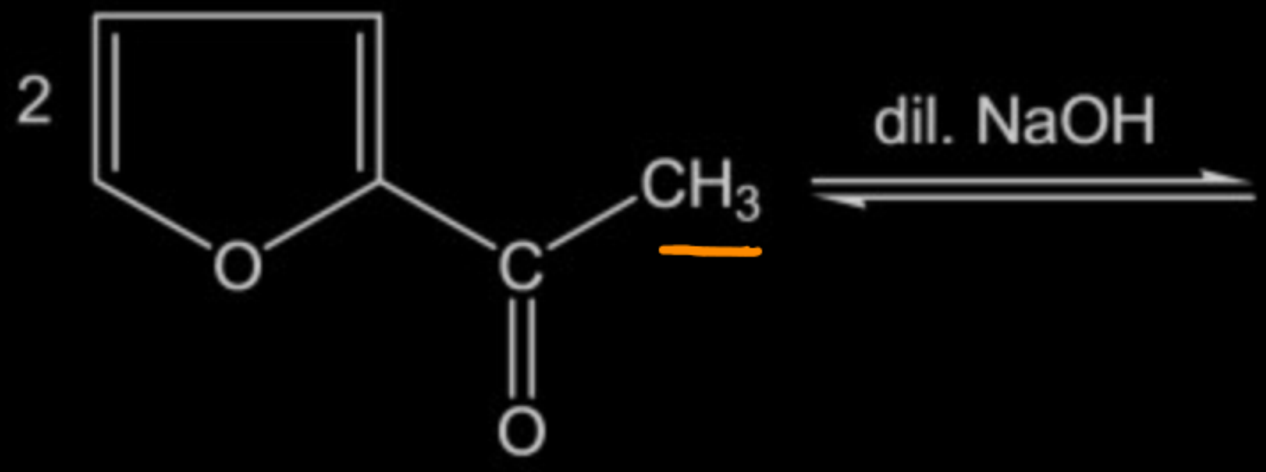


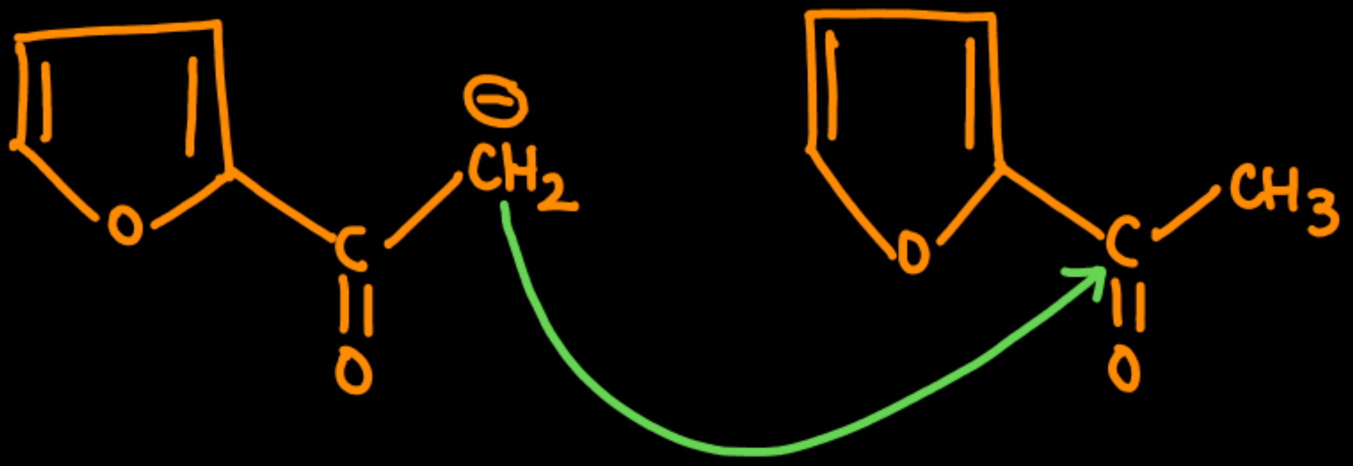
α,β unsaturated carbonyl
aldol condensation

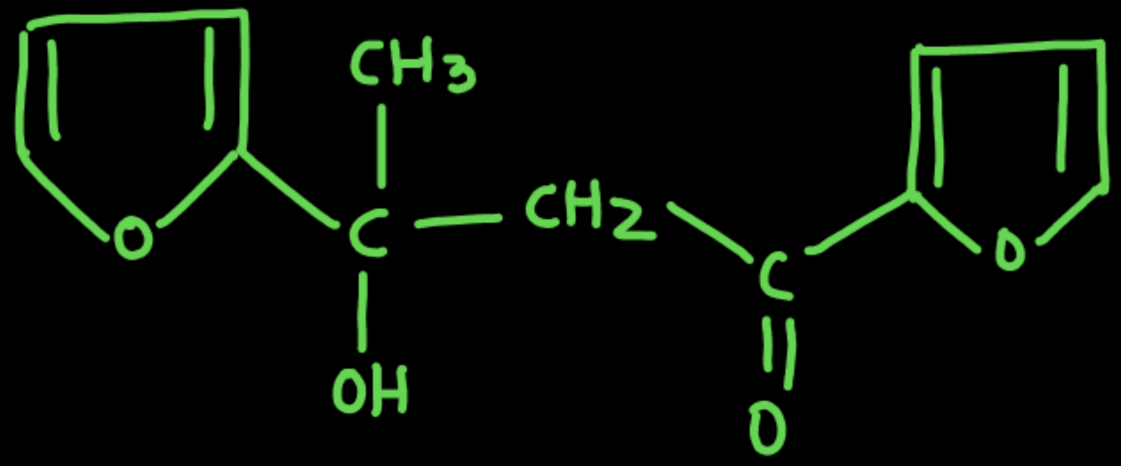


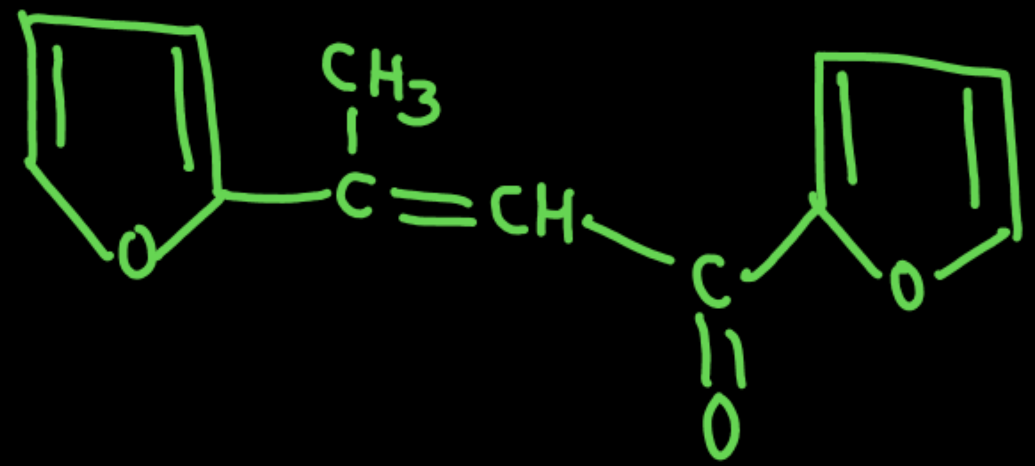
Ques.

2 mole carbonyl $\xrightleftharpoons{\text{dil base}}$ aldol
"must have αH"









$$2\,CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + \text{dil NaOH} \rightleftharpoons \overset{\ominus}{C}H_2-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

β hydroxy Carbonyl

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-CH_3$$

α-β unsaturated Carbonyl

inter aldol

Mixed or Cross aldol condensation: -

(i) Aldehyde – Aldehyde

$$\underset{\alpha H}{CH_3}-\overset{O}{\overset{\|}{C}}-H + CH_3-\underset{\alpha H}{CH_2}-\overset{O}{\overset{\|}{C}}-H \xrightarrow[(ii)\ OH^-/\ \Delta]{(i)\ dil.NaOH}$$

$$\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H \quad + \quad CH_3-\overset{\ominus}{C}H-\overset{O}{\overset{\|}{C}}-H$$

$$CH_3-\overset{O}{\overset{\|}{C}}-H \quad + \quad CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$$

1. $CH_3-\underset{\beta}{\overset{OH}{\overset{|}{C}H}}-\underset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-H$ Self aldol

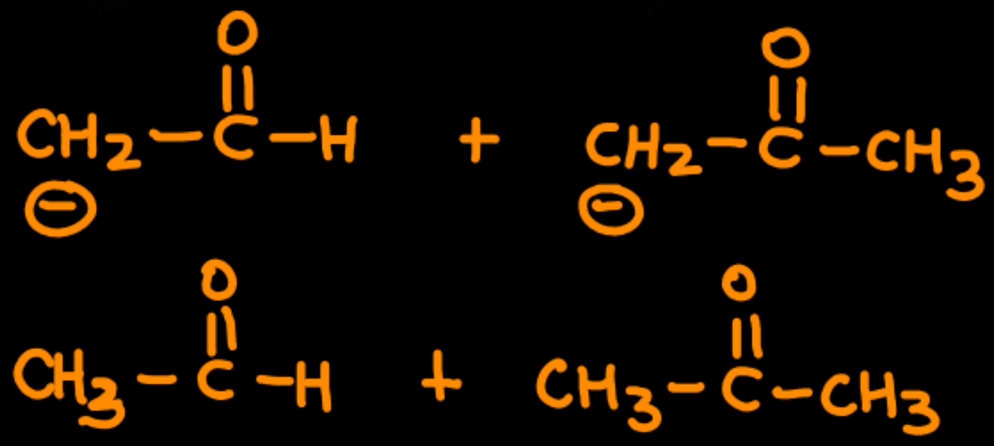
2. $CH_3-CH_2-\underset{\beta}{\overset{OH}{\overset{|}{C}H}}-\overset{\alpha}{\underset{CH_3}{\underset{|}{C}H}}-\overset{O}{\overset{\|}{C}}-H$ Self aldol

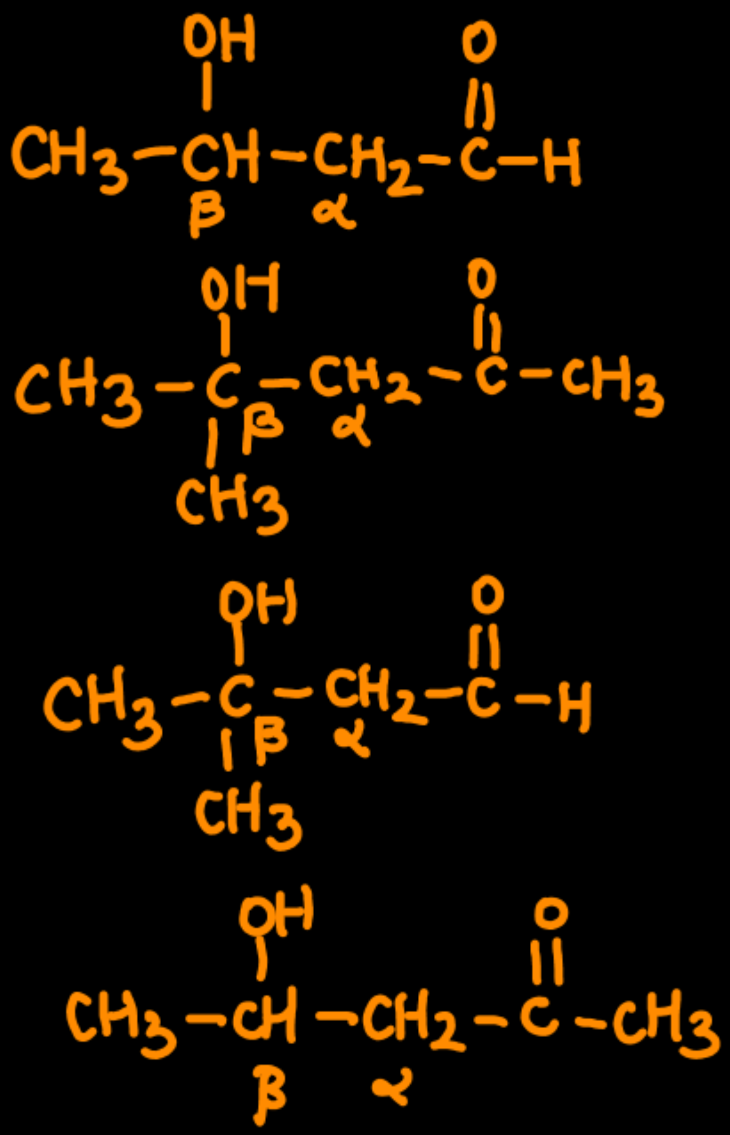
3. $CH_3-CH_2-\underset{\beta}{\overset{OH}{\overset{|}{C}H}}-\overset{\alpha}{C}H_2-\overset{O}{\overset{\|}{C}}-H$ Cross aldol

4. $CH_3-\underset{\beta}{\overset{OH}{\overset{|}{C}H}}-\overset{\alpha}{\underset{CH_3}{\underset{|}{C}H}}-\overset{O}{\overset{\|}{C}}-H$ Cross aldol

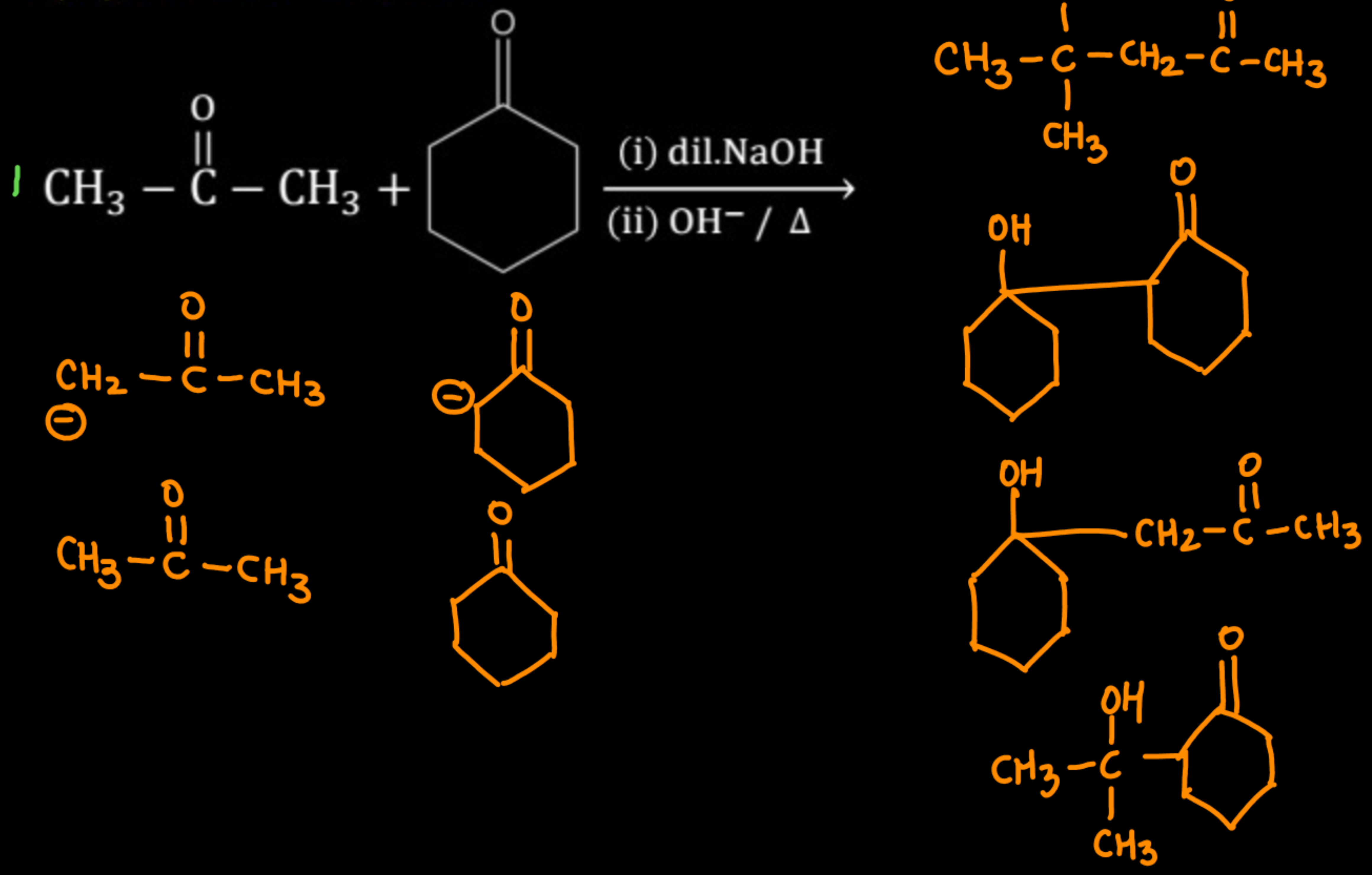
(ii) Aldehyde – Ketone

$$CH_3-\overset{\overset{O}{\parallel}}{C}-H + CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3 \xrightarrow[\text{(ii) } OH^- / \Delta]{\text{(i) dil.NaOH}}$$

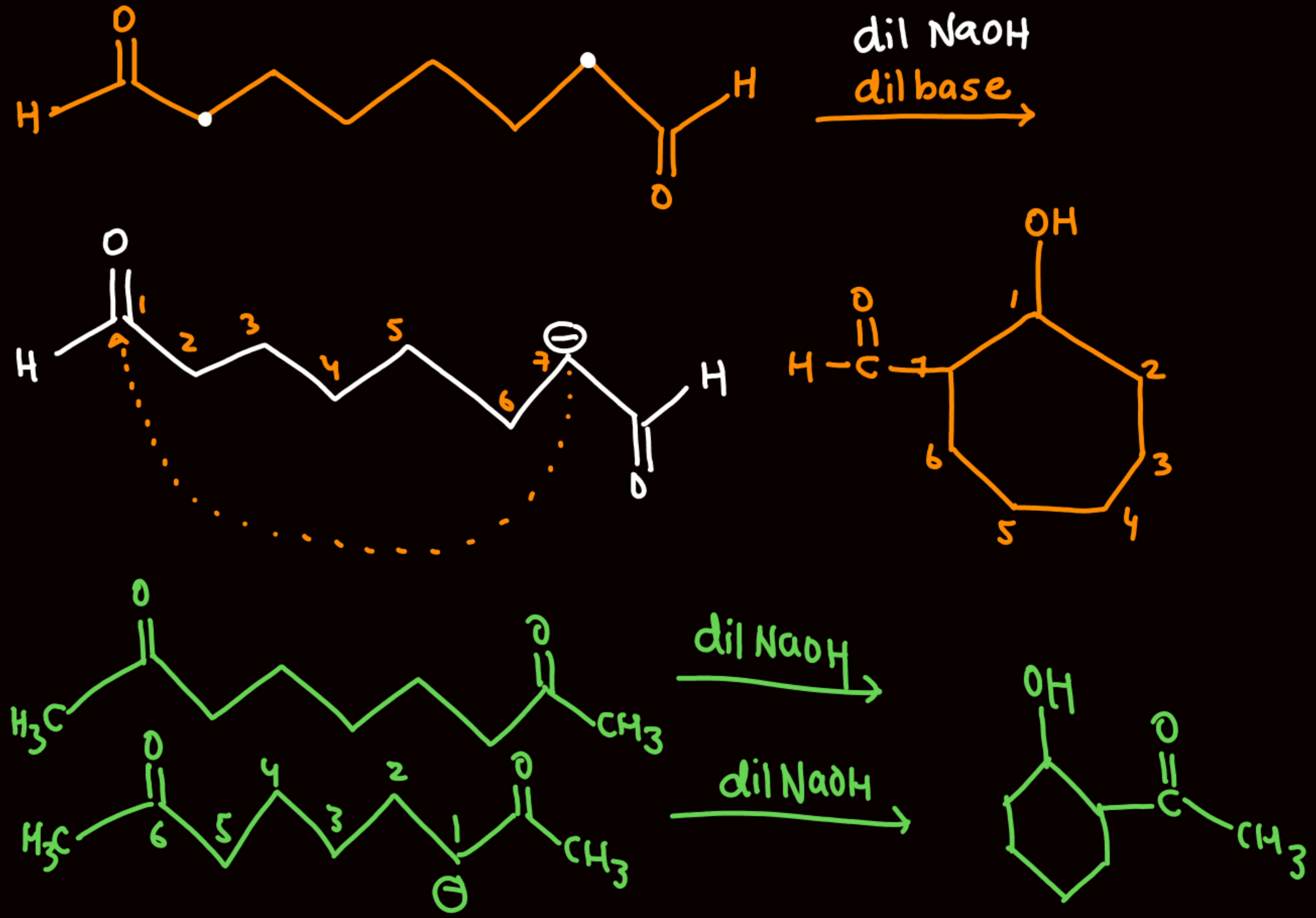




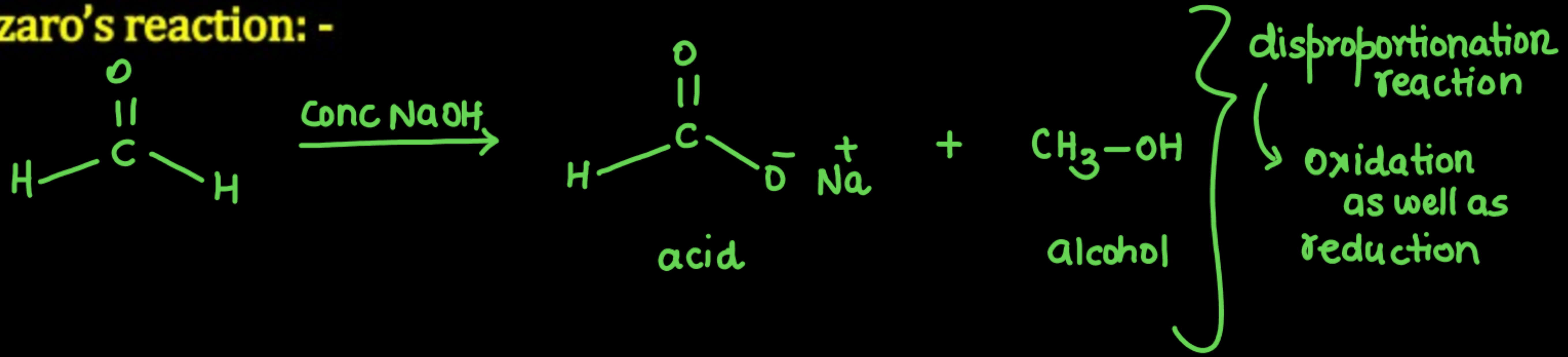
(iii) Ketone – Ketone



Intramolecular aldol



(3) Cannizaro's reaction: -

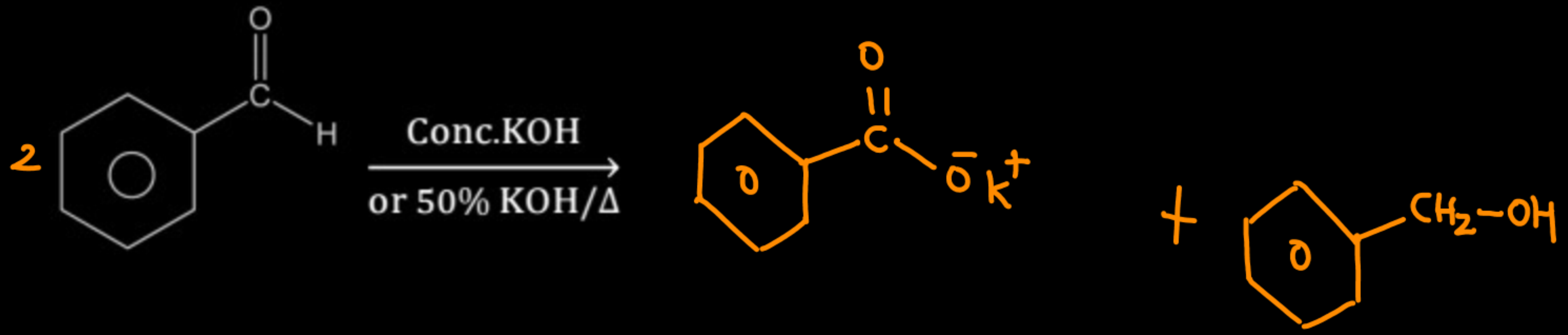


Examples:

(I) $$H-\overset{\overset{\large O}{\|}}{C}-H + H-\overset{\overset{\large O}{\|}}{C}-H \xrightarrow[\text{or 50\% KOH}/\Delta]{\text{Conc.KOH}} H-\overset{\overset{\large O}{\|}}{C}-\bar{O}\,K^{+} + CH_3-OH$$

acid — Oxidation

alcohol — Reduction

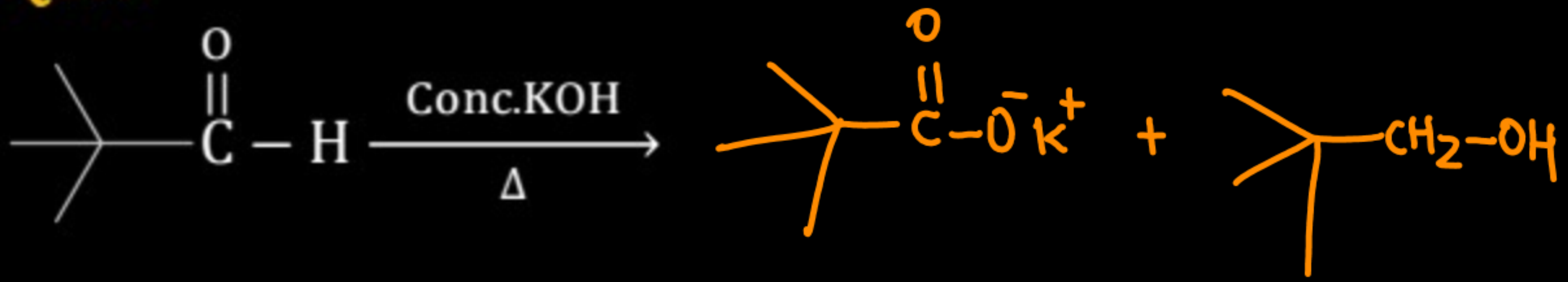
(II)


Ques.

$$H-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow[\Delta]{Conc.KOH} Ph-\overset{O}{\overset{\|}{C}}-O^{-}K^{+} + Ph-CH_2-OH$$

oxidation   Reduction

Ques.



Ques.

$$H-\overset{\overset{\large O}{\|}}{C}-D \xrightarrow[\Delta]{\text{Conc.KOH}} D-\overset{\overset{\large O}{\|}}{C}-\bar{O}\,K^{+} + D-CH_2-OH$$

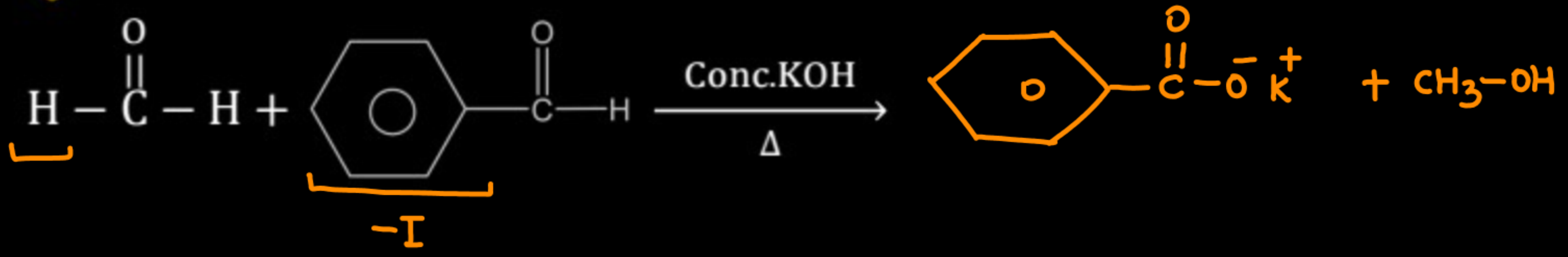
(H–C bond) ↓ easily break



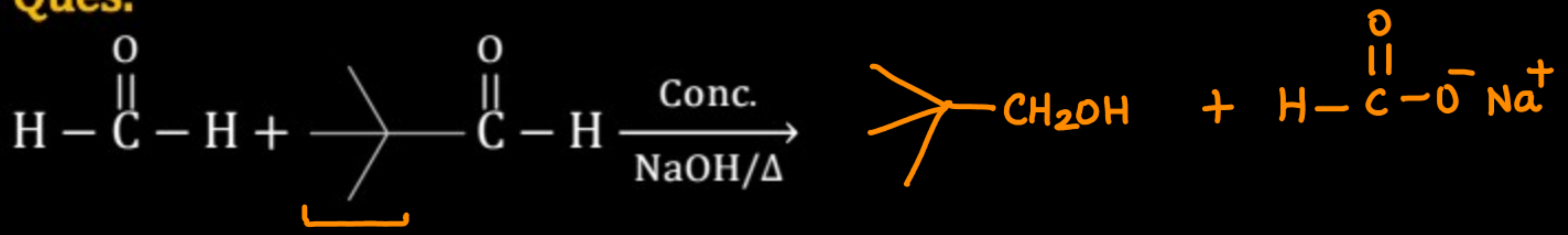
Carbonyl containing EWG is oxidised more & viceversa.
EDG is Reduced.

Cross – Cannizaro's reaction: -

Ques.



Ques.



Ques.

$$Ph-\overset{O}{\overset{\|}{C}}-H + NO_2-Ph-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{NaOH}/\Delta]{\text{Conc.}} Ph-CH_2-OH + NO_2-Ph-\overset{O}{\overset{\|}{C}}-O^-K^+$$

More EWG



Ques.

$$\underbrace{MeO} - Ph - \overset{\overset{O}{\|}}{C} - H + Ph - \overset{\overset{O}{\|}}{C} - H \xrightarrow[NaOH/\Delta]{Conc.} MeO-Ph-CH_2OH + Ph-\overset{\overset{O}{\|}}{C}-\bar{O}Na^{+}$$

Test of Aldehyde & Ketone

1. Tollen Test → Gives test with Aliphatic & Aromatic aldehyde (ketone ✗)
2. Fehling Test → " " " only aliphatic aldehyde (Aromatic ✗) (ketone ✗)
3. Benedict Test
4. 2,4 DNP Test

(1) Tollen's Test: (mild oxidising agent)

Tollen's Reagent → Ammonical Silver nitrate

→ $NH_4OH + AgNO_3$

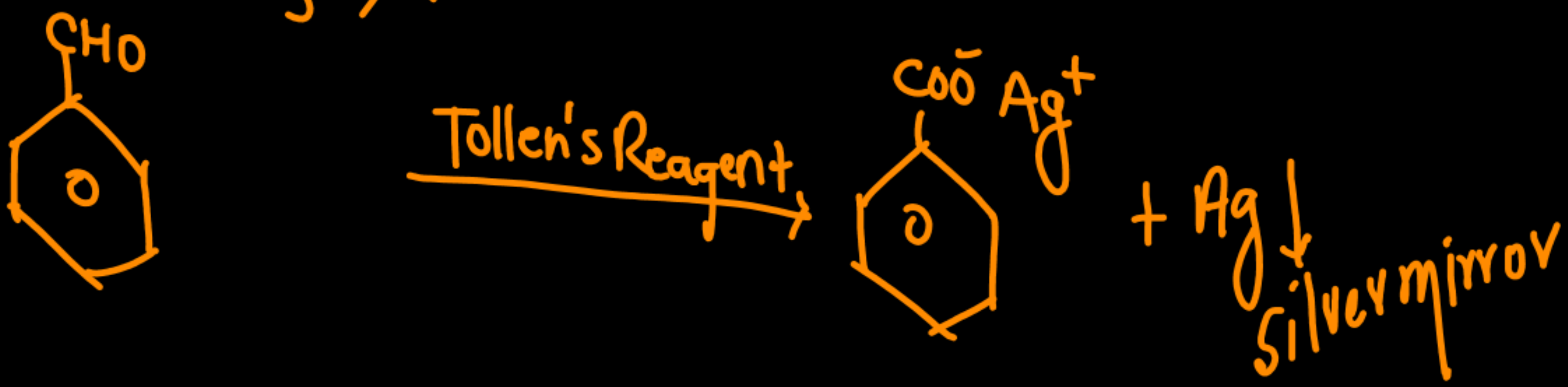
→ $[Ag(NH_3)_2]OH$



$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{Tollen's Reagent}} CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\,\overset{+}{Ag} + Ag\downarrow$$

Silver mirror

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \quad \times$$

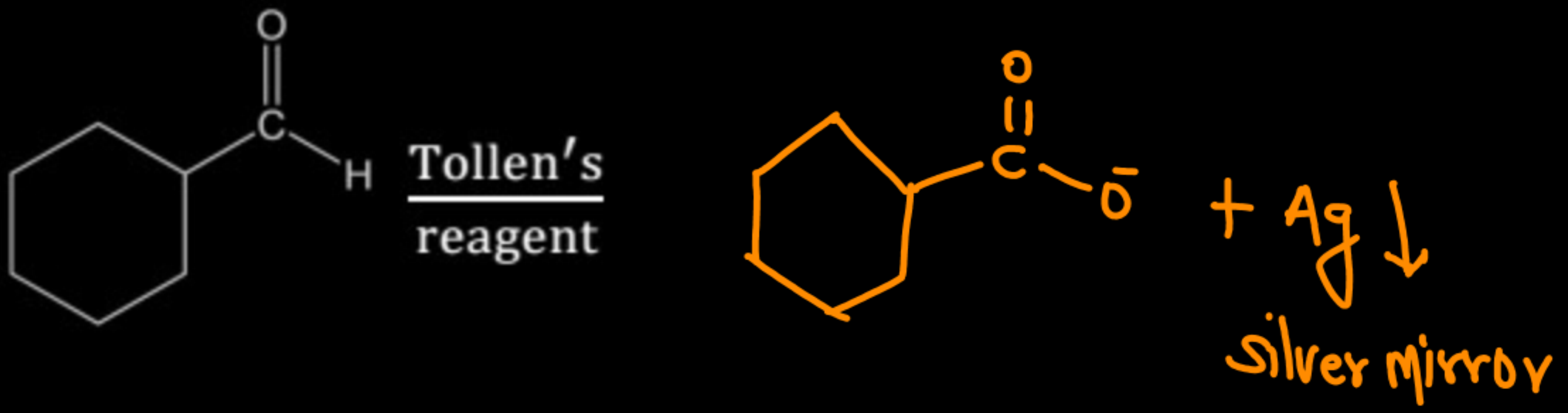


Ques.

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-H + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow R-\overset{\displaystyle O}{\overset{\|}{C}}-\bar{O} \quad + \quad Ag\downarrow$$

Silver Mirror

Ques.



Ques.

$$R-\overset{\overset{\large O}{\|}}{C}-R \xrightarrow[\text{reagent}]{\text{Tollen's}} ✗$$

(2) Fehling's Test:

Fehling Soln A → aq soln of $CuSO_4$

Fehling Soln B → Sodium potassium tartarate

$$
\begin{array}{l}
HO-CH-COO^-\,Na^+ \\
\quad\;\;\;| \\
HO-CH-COO^-\,K^+
\end{array}
$$

aliphatic aldehyde → ✓

aromatic aldehyde → ✗

Ketone → ✗

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{Fehling soln}} R-\overset{O}{\overset{\|}{C}}-\bar{O} + Cu_2O\downarrow$$

Red brown ppt

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{\;\;''\;\;} ✗$$



$\xrightarrow{\;\;''\;\;}$ ✗

Benedict Test

Benedict Soln → mix of $CuSO_4$ + Sodium citrate + NaOH

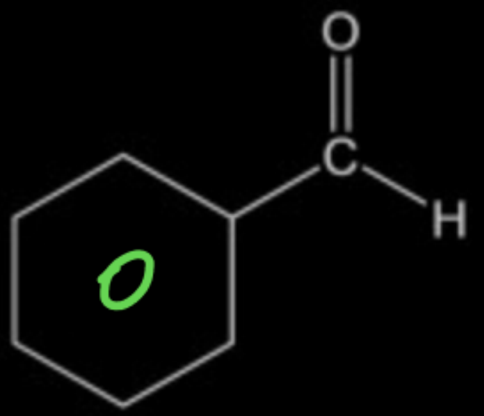
$$RCHO \xrightarrow{BS} RCOO^- + Cu_2O\downarrow$$

Red Brown ppt

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\text{reagent}]{\text{fehling's}} \quad ✓$$

Ques.



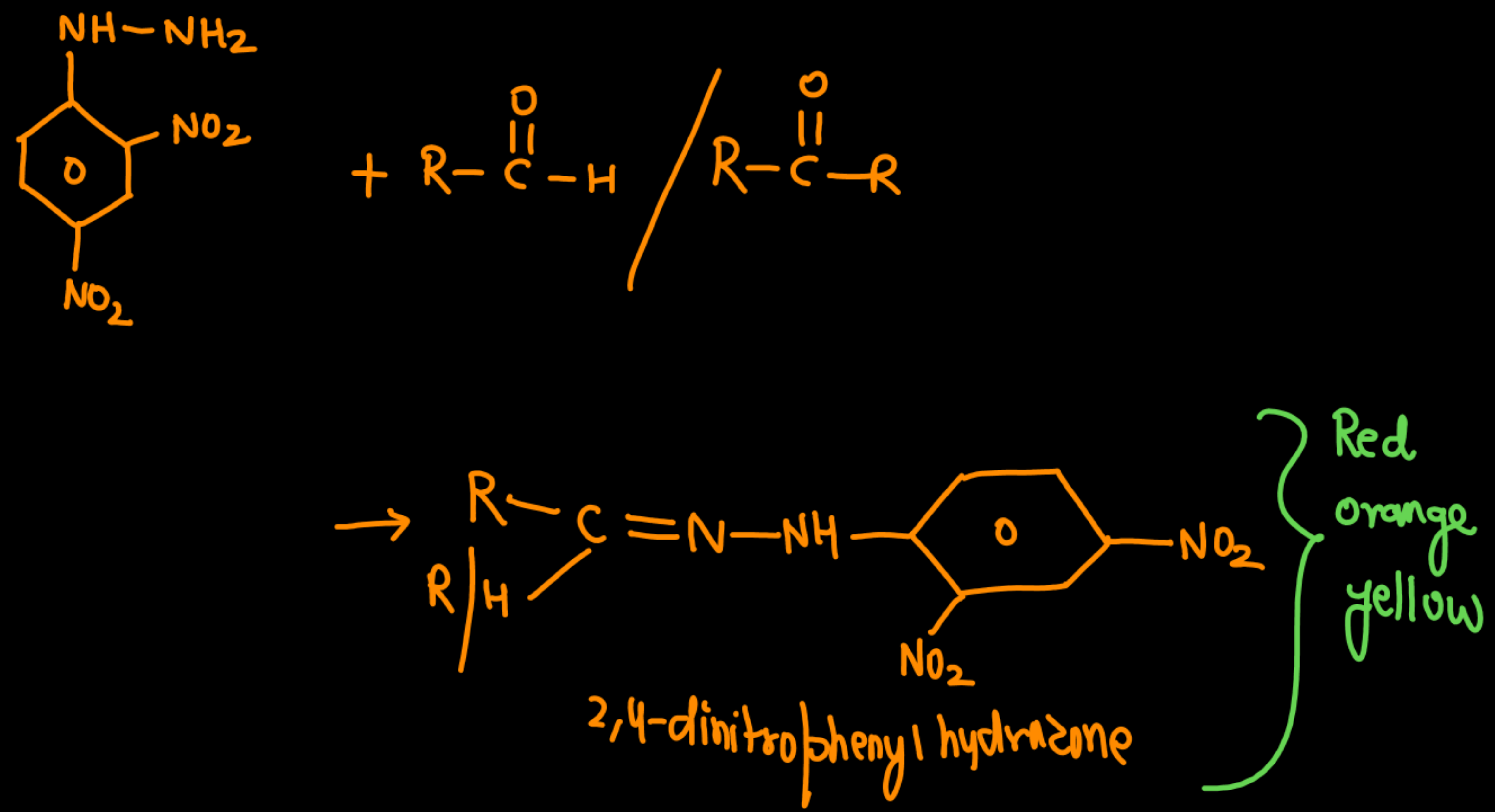
$$\xrightarrow[\text{reagent}]{\text{fehlng's}} \quad ✗$$

Ques.

$$R-\overset{\overset{\large O}{\|}}{C}-R \xrightarrow[\text{reagent}]{\text{fehling's}} \text{X}$$

2,4-DNP test:

2,4 dinitrophenylhydrazine





Method of Preparation

(i) From alkene }
(ii) —— alkyne } oxidative ozonolysis

(iii) —— Alkyl Benzene ⟶ PPCH oxidation

(iv) —— Alcohol } oxid^{n}

(v) —— Aldehyde } oxid^{n}

(vi) ⟵ Nitrile } Hydrolysis

(vii) —— Amide } Hydrolysis

(viii) —— acid halide & acid anhydride } Hydrolysis

(ix) —— Ester } Hydrolysis

(1) Oxidation of Alkene (Oxidative ozonolysis):

$$\xrightarrow[H_2O]{O_3}$$

Ques.

$$RCH = CHR' \xrightarrow{O_3/H_2O} RCHO + R'CHO$$

$$RCHO \rightarrow RCOOH \qquad R'CHO \rightarrow R'COOH$$

Ques.

$$RCH = CHR' \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Conc.} KMnO_4/OH^-} RCHO + R'CHO$$

$$RCHO \rightarrow RCOOH \qquad R'CHO \rightarrow R'COOH$$

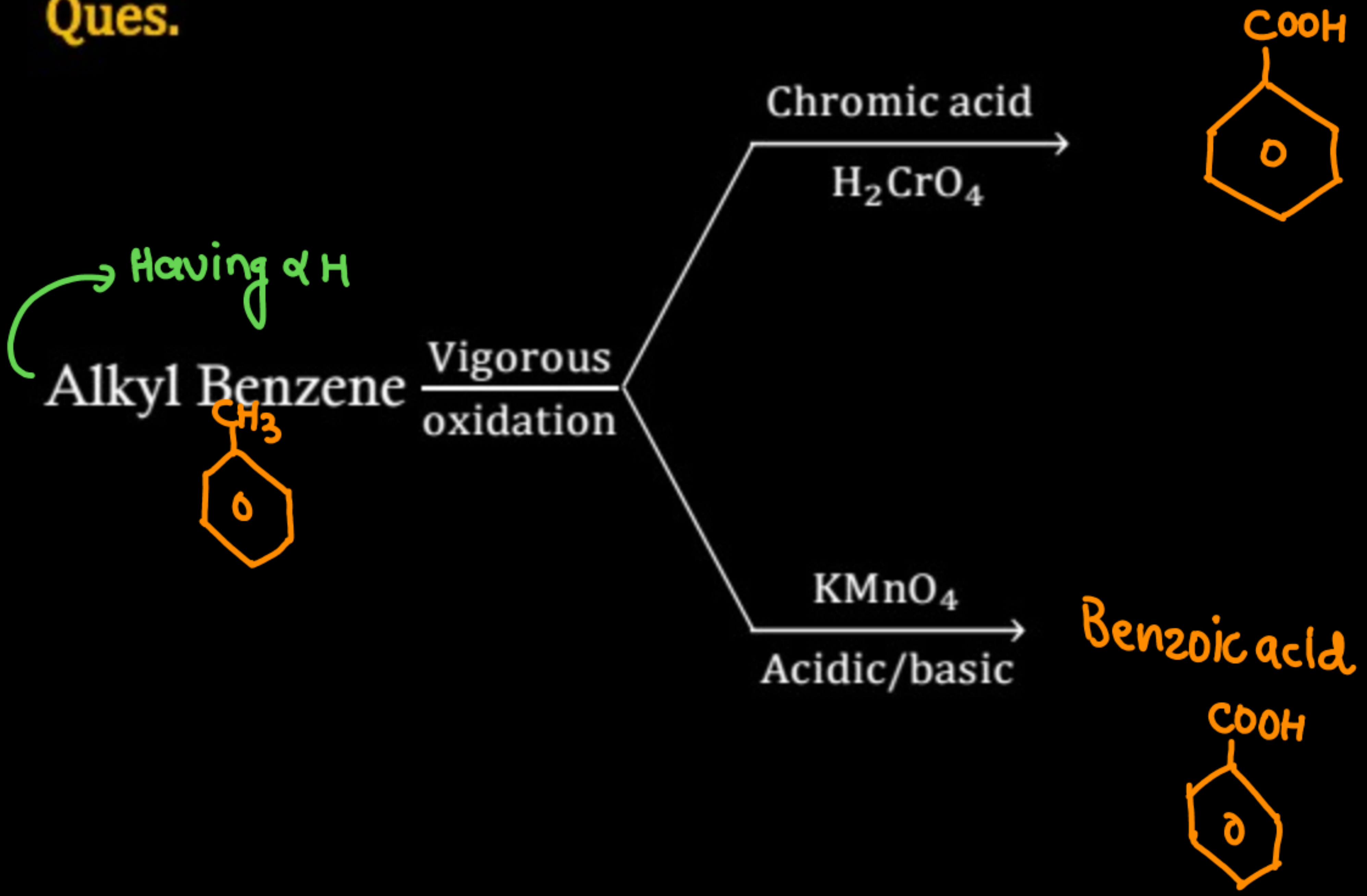
(2) Oxidative ozonolysis of Alkyne:

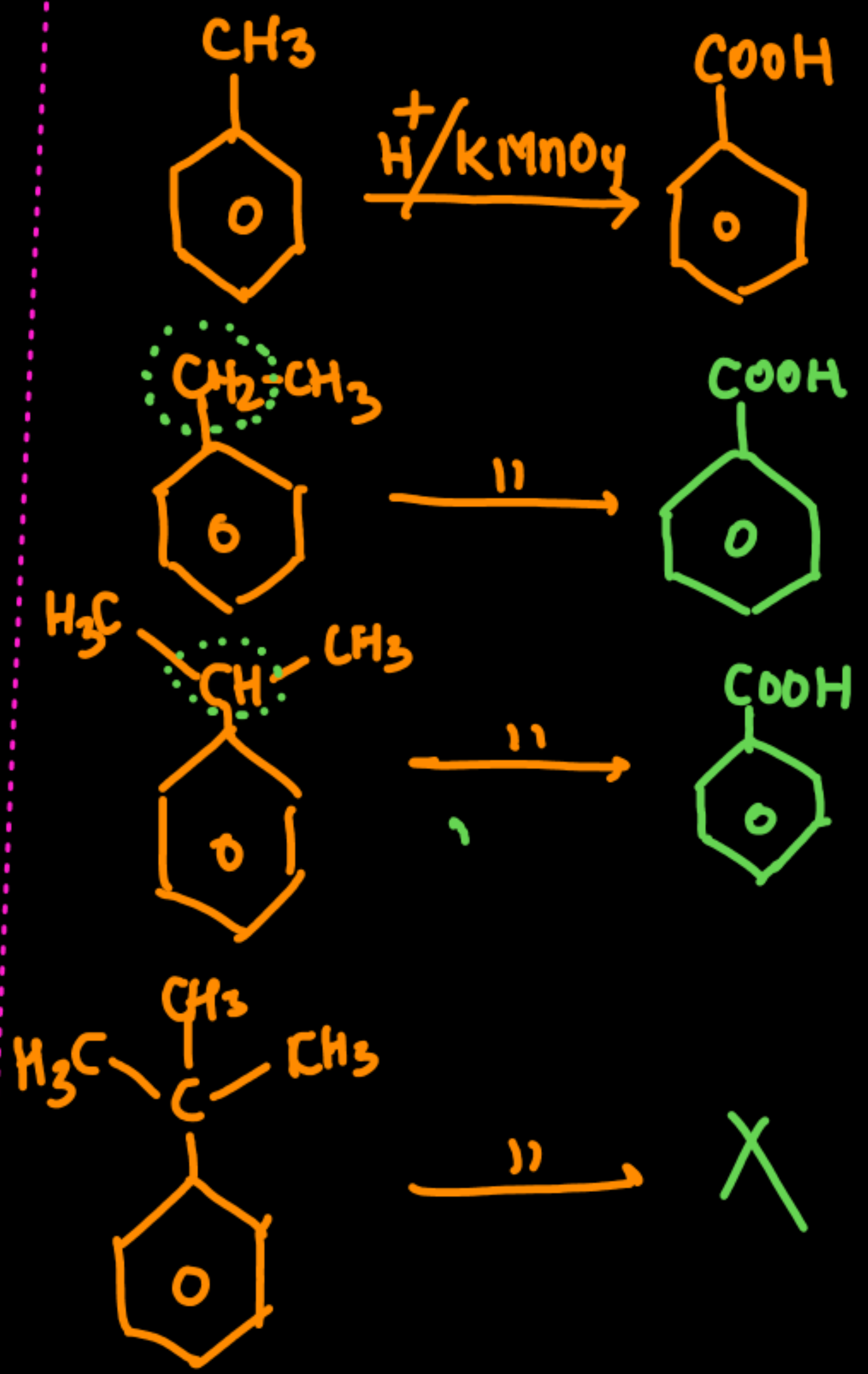
Ques.

$$R - C \equiv CH \xrightarrow{O_3/H_2O} RCOOH + HCOOH$$

(3) Alkyl Benzne

Ques.





(4) Alcohol ⟶ Acid:

Ques.

$$R - CH_2 - OH \xrightarrow[\text{basic/neutral}]{KMnO_4/\text{Acidic}} R-COOH$$

Ques.

$$R - CH_2 - OH \xrightarrow{H^+/K_2Cr_2O_7} R-COOH$$

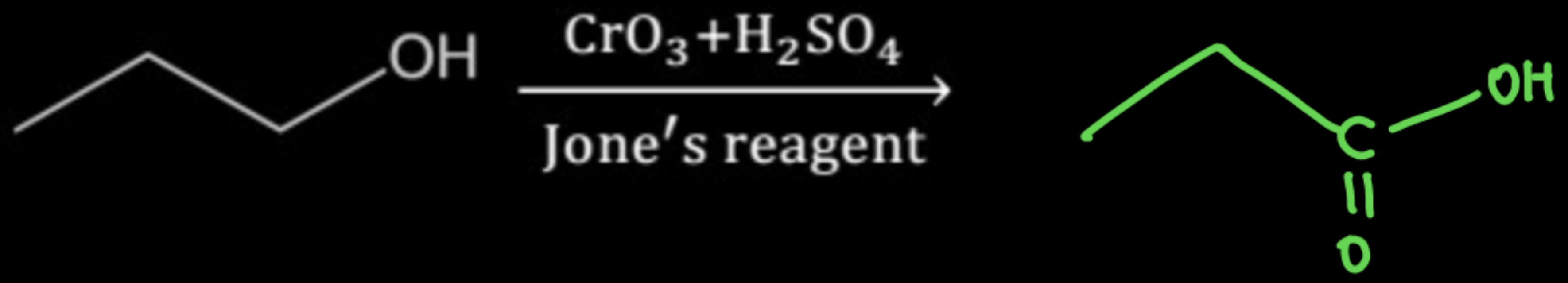
Ques.

$$R-CH_2-OH \xrightarrow[(CrO_3+H_2SO_4)]{\text{Jones reagent}} RCOOH$$

Ques.

$$CH_3(CH_2)_8CH_2OH \xrightarrow[\text{Jone's reagent}]{CrO_3+H_2SO_4} CH_3(CH_2)_8COOH$$

Ques.



(5) Aldehyde ⟶ Acid:

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{KMnO_4\ /\ H^+\ /\ OH^-\ /\ \text{neutral}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{H^+/K_2Cr_2O_7} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{CrO_3+H_2SO_4\ \text{Jone's reagent}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{\text{Tollen's reagent}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{\text{Fehling's reagent}} RCOOH$$

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{\text{Benedicts solution}} RCOOH$$

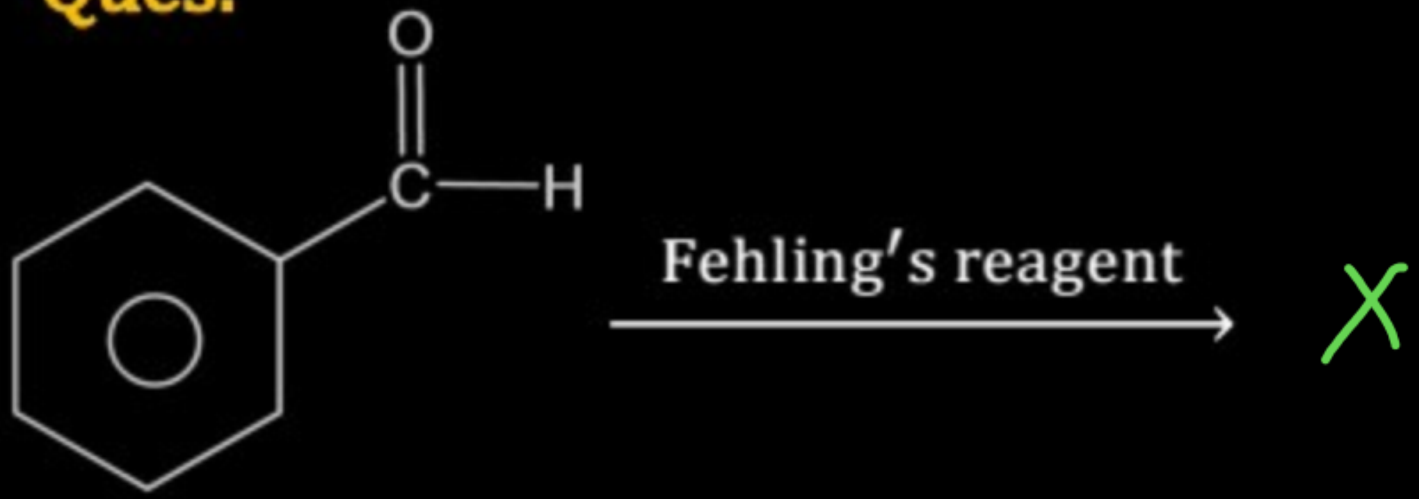
Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{\text{PCC, PDC}} RCOOH$$

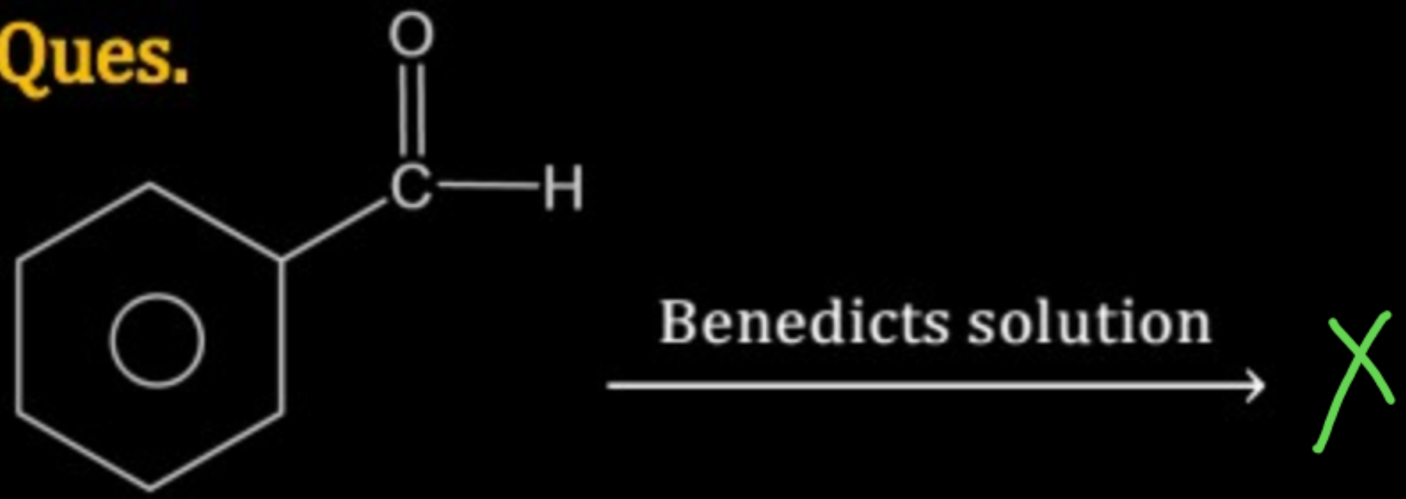
Ques.



Ques.



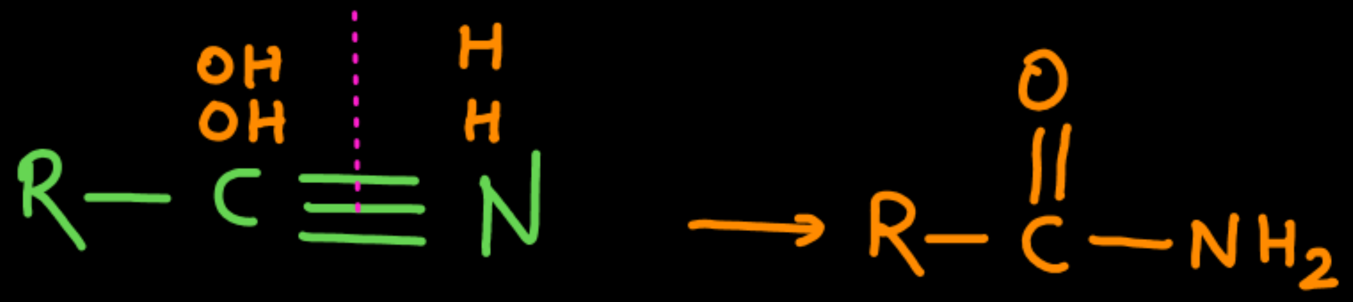
Ques.



(6) Nitrile ⟶ Hydrolysis (Acid):

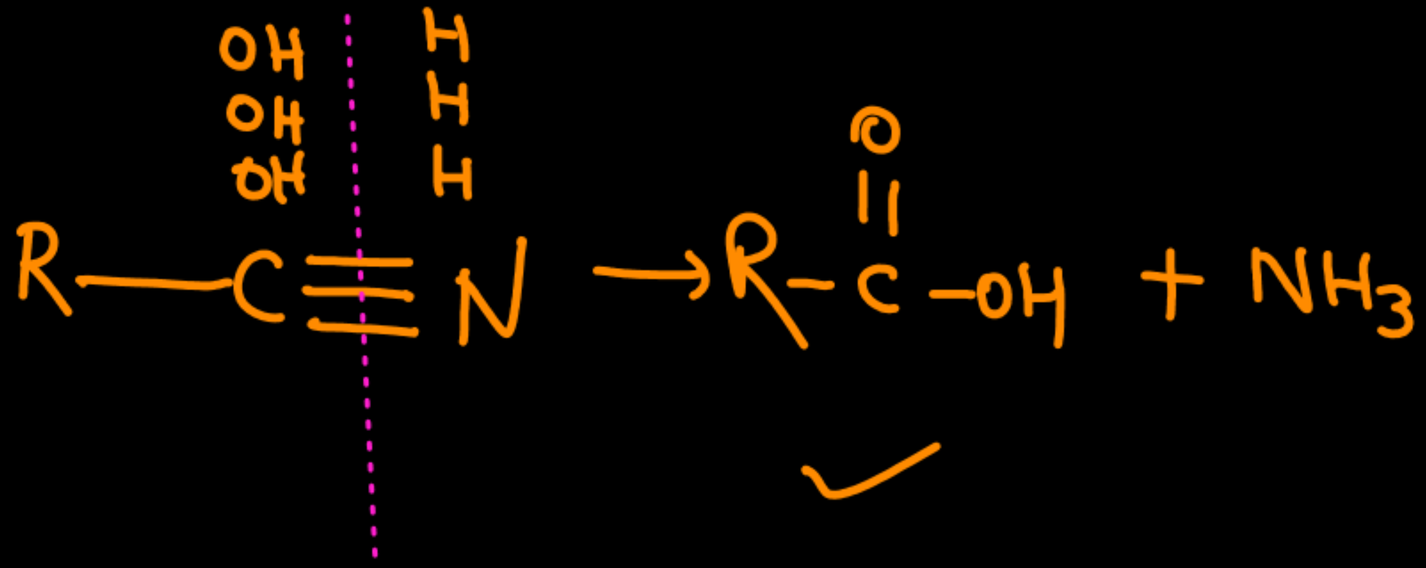
Ques.

$$R-C\equiv N \xrightarrow{\text{Partial hydrolysis}}$$

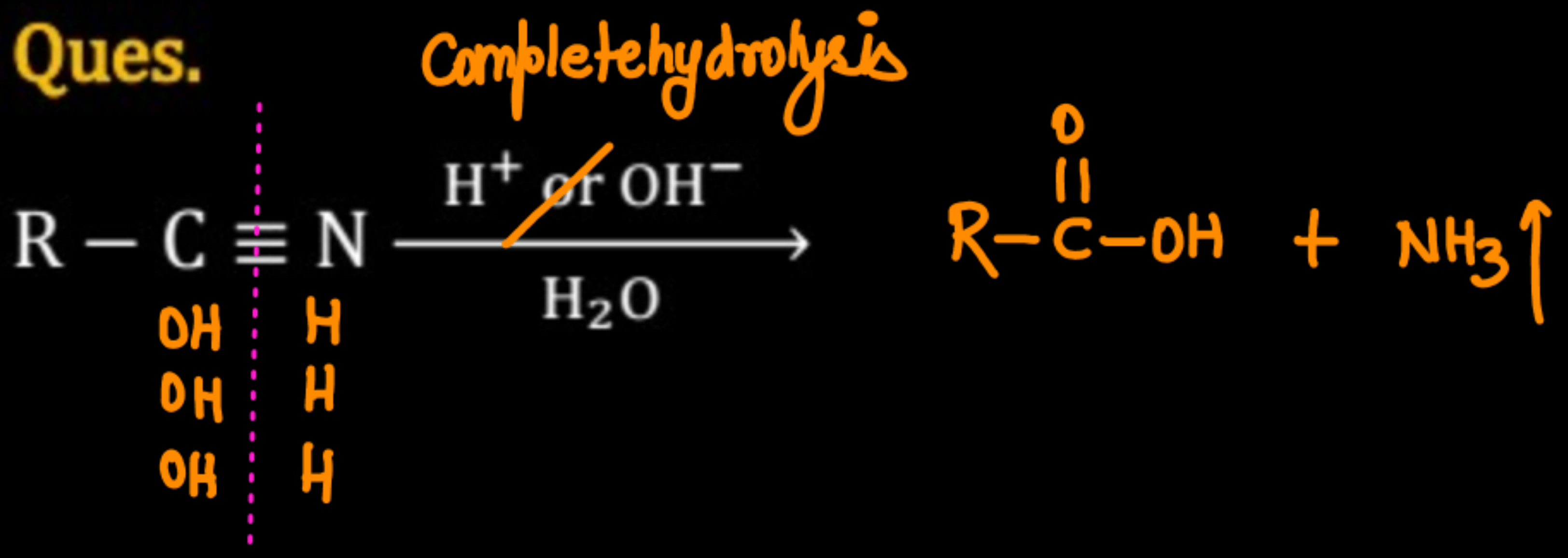


Ques.

$$R-C\equiv N \xrightarrow{\text{Complete hydrolysis}}$$



Ques.

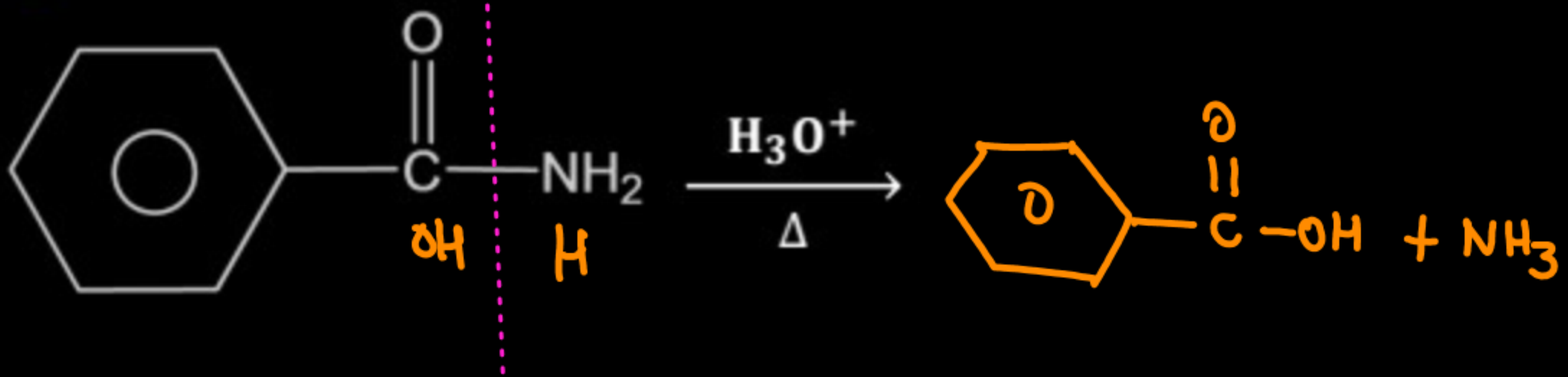


(7) Amide ⟶ Hydrolysis (Acid):

Ques.

$$CH_3-\overset{\overset{\large O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{H_3O^+} CH_3-\overset{\overset{\large O}{\|}}{C}-OH + NH_3$$

Ques.



(8) Acyl halide & Acyl anhydride ⟶ Hydrolysis (Acid):

Ques.

$$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[\text{or } H_2O/H^+]{H_3O^+} R-\overset{\overset{O}{\|}}{C}-OH + HCl$$

OH H

Ques.

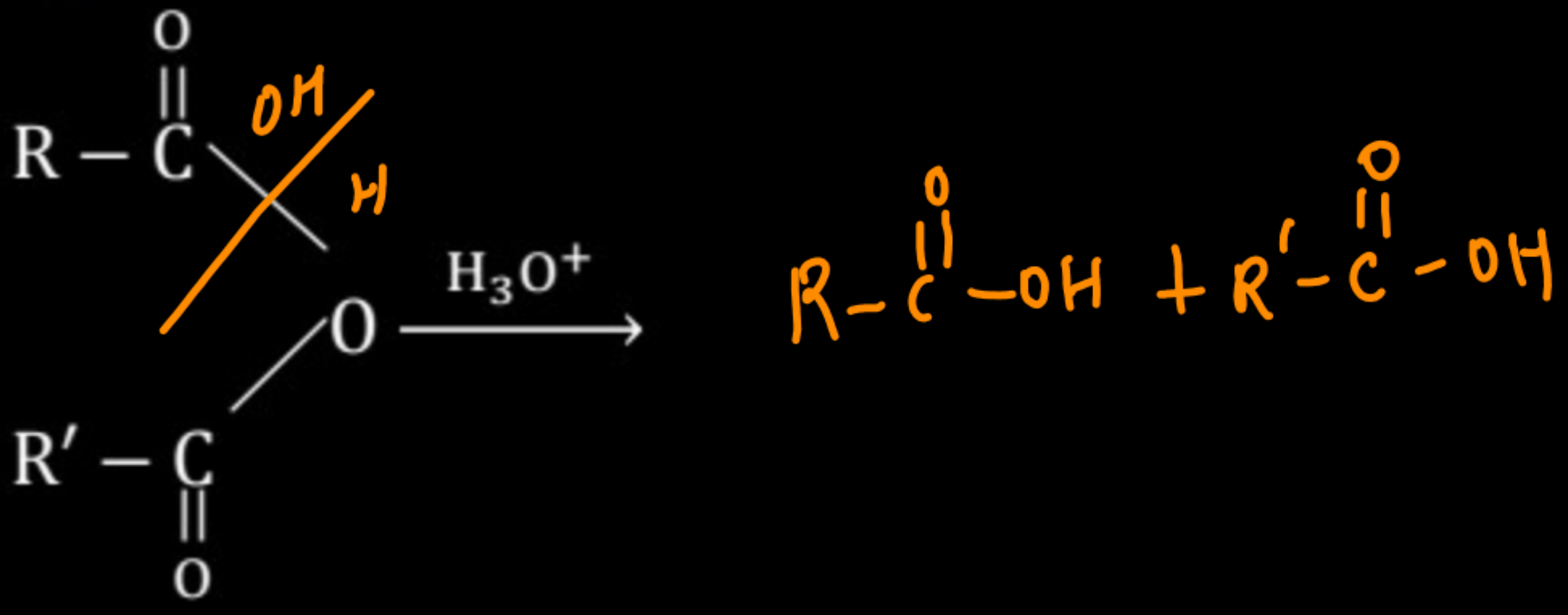
$$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[OH^-]{H_2O} R-\overset{\overset{O}{\|}}{C}-OH + HCl$$

OH H

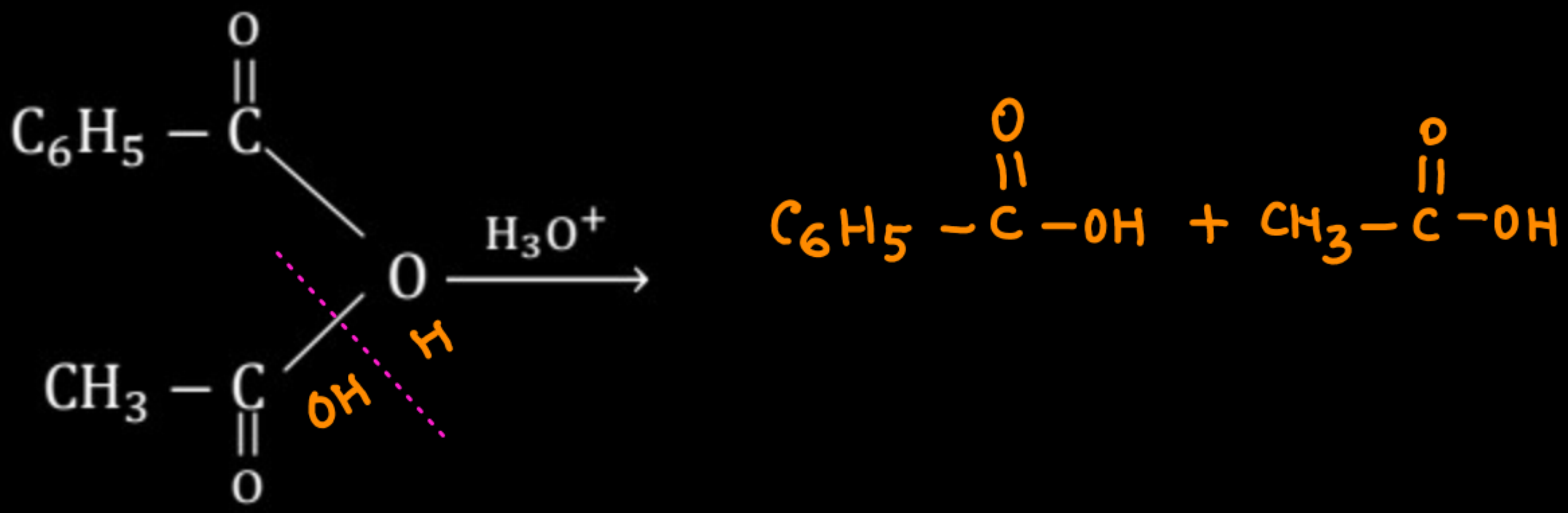
Ques.

$$CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-Br \xrightarrow[H_2O]{H_2SO_4} CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-OH + HBr$$

Ques.



Ques.

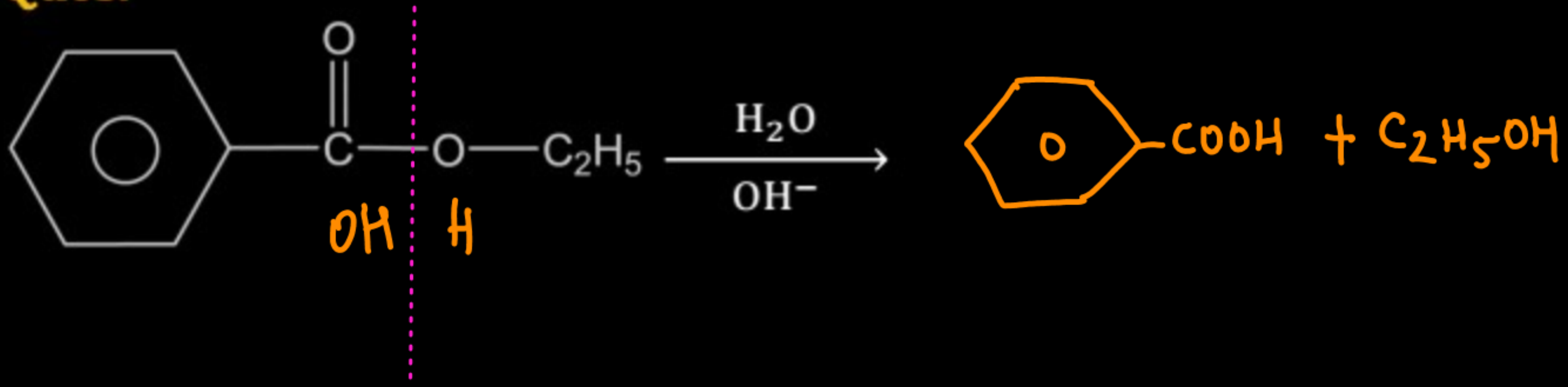


(9) Ester $\xrightarrow{\text{Hydrolysis}}$ Acid

Ques.

$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5 \xrightarrow[H^-]{H_2O} CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH + C_2H_5-OH$$

Ques.



Chemical Reaction

1. Reaction with PCl_5 , PCl_3, $SOCl_2$, SO_2Cl_2
2. Esterification Rx^n
3. Rx^n with NH_3

Esterification

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'-OH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2O$$

Ester

Ester

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{*}{O}H + Ph-\overset{18}{O}H \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{18}{O}-Ph + H_2\overset{*}{O}$$

Ester

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{PCl_5} R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + HCl + POCl_3$$

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{PCl_3} R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_3PO_3 + HCl$$

Ques.

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{darzen Rxn}]{SOCl_2} R-\overset{O}{\overset{\|}{C}}-Cl + SO_2\uparrow + HCl\uparrow$$

Ques.

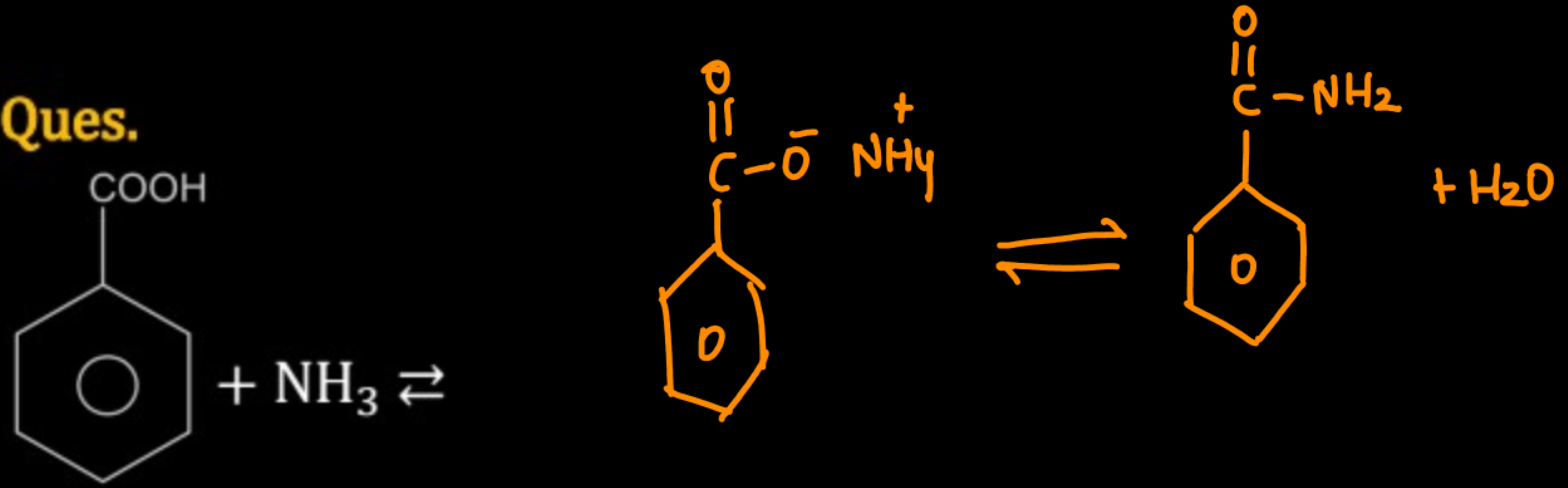
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SO_2Cl_2} R-\overset{O}{\overset{\|}{C}}-Cl + SO_3\uparrow + HCl\uparrow$$

Examples:

Ques.

$$CH_3-\overset{O}{\overset{\|}{C}}-OH+\underset{\text{base}}{\ddot{N}H_3}\rightleftarrows CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\;\overset{+}{N}H_4\xrightleftharpoons{-H_2O}CH_3-\overset{O}{\overset{\|}{C}}-NH_2+H_2O$$

Ques.



Reaction involving –COOH group: -

(1) Reduction:

Ques.

$$R - \overset{\overset{O}{\|}}{C} - OH \xrightarrow[\text{Strong Reducing Agent}]{LiAlH_4} R - CH_2 - OH$$

Acid   Alcohol

(2) Decarboxylation:

Ques.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[CaO]{NaOH} R-H + CO_2\uparrow$$

NaOH → Caustic soda (3:1)

CaO → Quicklime

Sulphuric acid

Hydrazoic acid

(3) Schmidt Reaction:

Carboxylic acid

Ques.

$$R-\overset{\overset{O}{\|}}{C}-OH + N_3H \xrightarrow[H_2SO_4]{Conc.} R-NH_2 + N_2\uparrow + CO_2\uparrow$$

amine

(4) Hunsicker Reaction:

Ques.

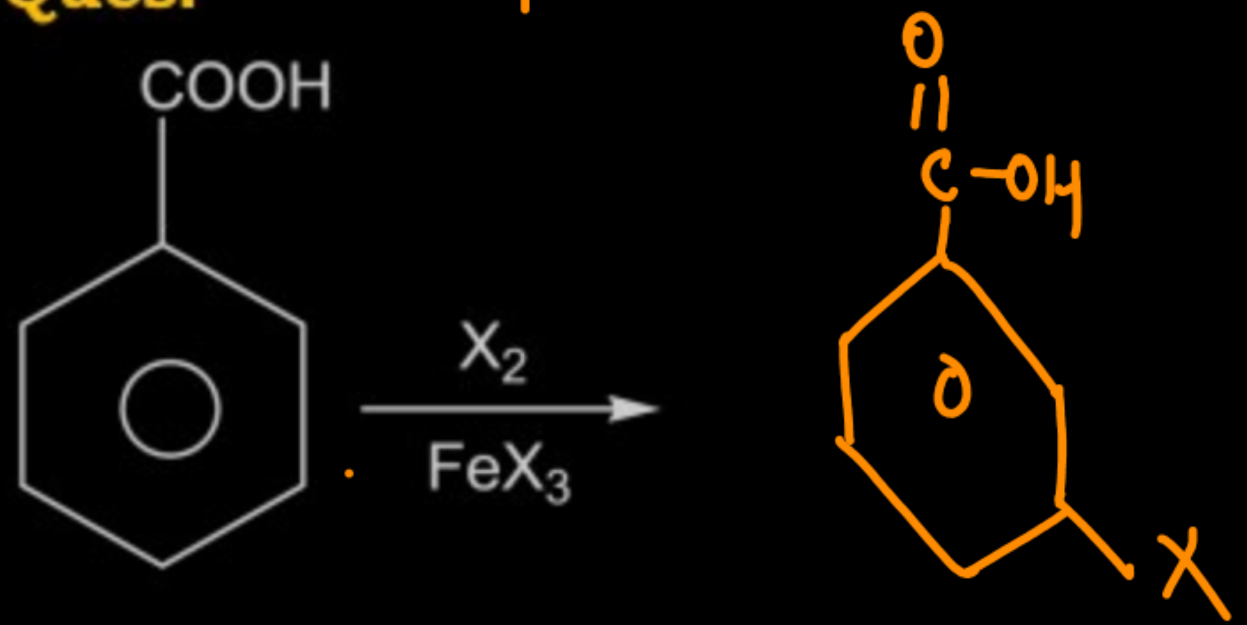
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{Ag_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-\bar{O}\,Ag^{+} \longrightarrow R-H + CO_2\uparrow$$

Ring Substitution:

Ques.



Ques.



THANK YOU
All the Best!!

Amines

Amines

Method of Preparation

1. Ammonolysis → Alkyl Halide; → Alcohol

$R-X + NH_3 \xrightarrow{-HX} R-NH_2 + NH_3 \longrightarrow R_2-NH + NH_3 \longrightarrow R_3\ddot{N}$

$R-NH_2$: 1° amine; R_2-NH: 2° amine; $R_3\ddot{N}$: 3° amine

$R_3\ddot{N} + NH_3 \longrightarrow \overset{-}{R_4}\overset{+}{N}$ Quatarnary amine

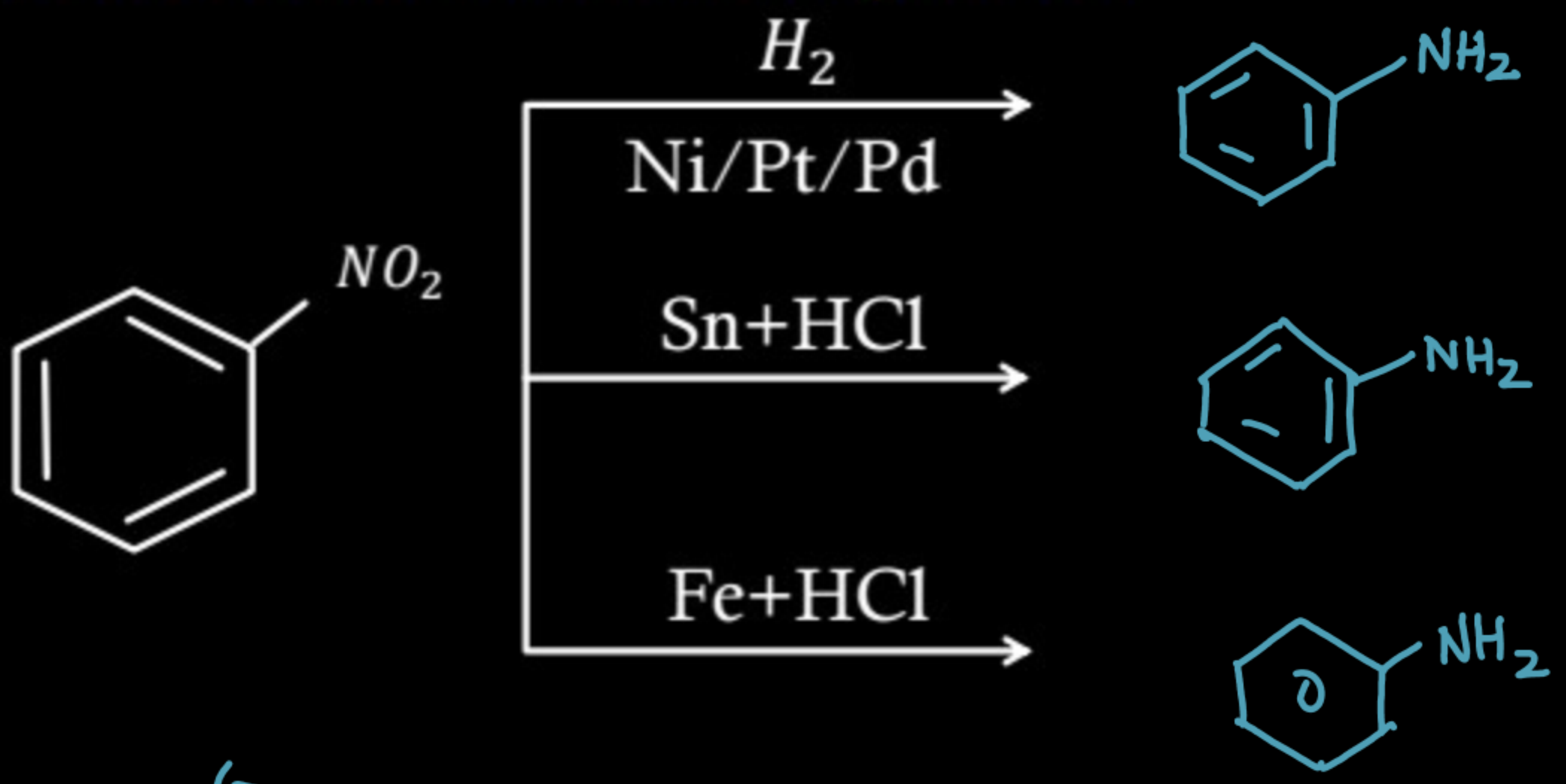
$R-OH + NH_3 \longrightarrow R-NH_2 + NH_3 \longrightarrow R_2NH + NH_3 \longrightarrow R_3N + NH_3 \longrightarrow \overset{-}{R_4}\overset{+}{N}$

1° amine, 2° amine, 3° amine, Quatarnary amine

2. Reduction of NO_2
3. Reduction of Nitrile & isonitrile
   - H_2/Ni or Pt or Pd
   - Sn + HCl
   - $LiAlH_4 / H_2O$
4. Reduction of amide & oxime
5. Hydrolysis of isocyanide & isocyanate
6. Gabriel pthalimide Reaction
7. Schmidt Reaction
8. Curtius Reaction

Reduction

i) Reduction of nitro compounds



→ (Fe+HCl) reaction is prefered because on hydrolysis it produces HCl again. So less amt of HCl is req in beginning.

Amines

ii) Reduction of nitrile

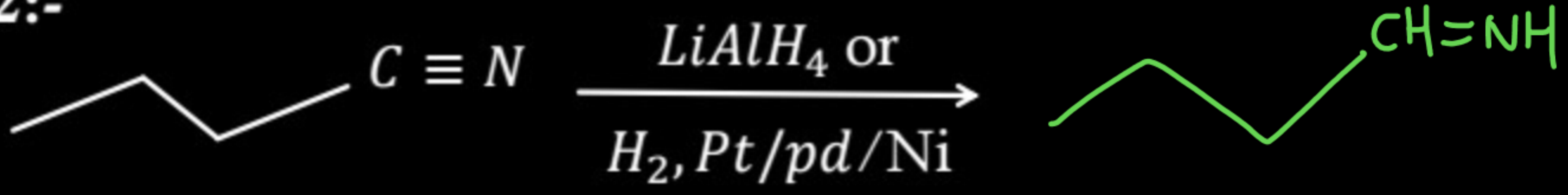
Q 1:-

$$R-C\equiv N \xrightarrow{H_2,\ Ni/Pt/Pd} R-CH=NH$$

$$R-C\equiv N \xrightarrow{LiAlH_4/H_2O} R-CH=NH$$

$$R-C\equiv N \xrightarrow{Sn + HCl} R-CH=NH$$

Q 2:-



Reduction of isonitrile

iii) Reduction of isonitrile

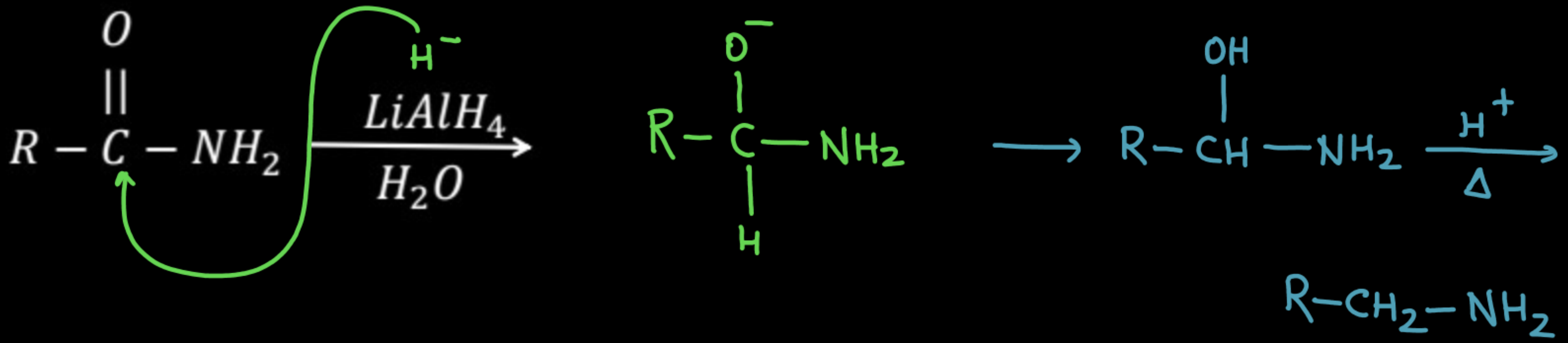
$$R-N\equiv C \xrightarrow{LiAlH_4} R-\overset{+}{N}H=CH_2$$

$$R-N\equiv C \xrightarrow{Sn+HCl} R-\overset{+}{N}H=CH_2$$

$$R-N\equiv C \xrightarrow{H_2, Ni/Pt/Pd} R-\overset{+}{N}H=CH_2$$

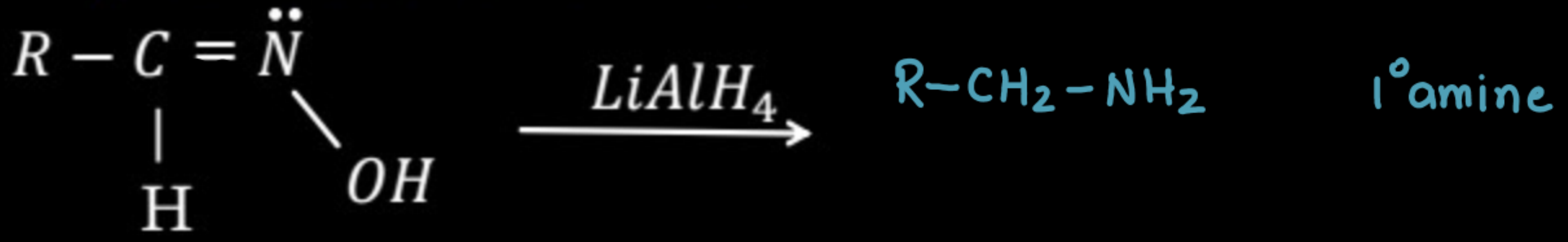
Amines

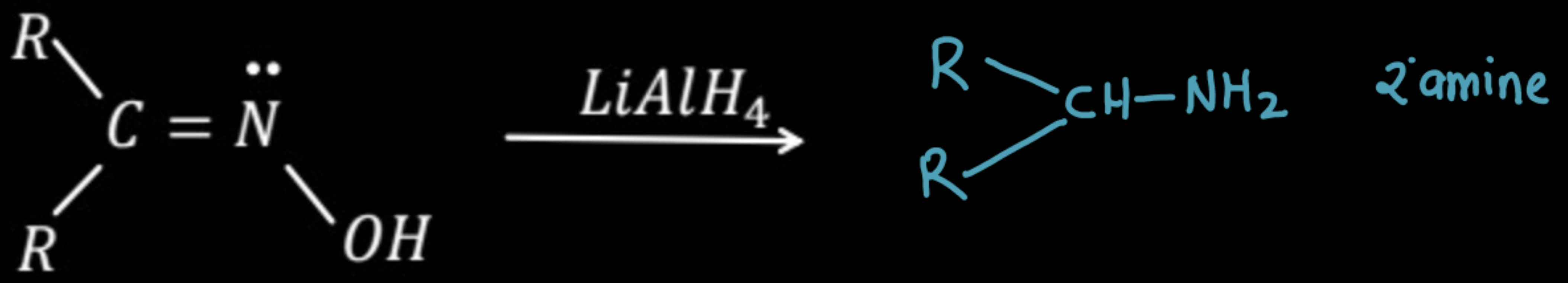
iv) Reduction of amide

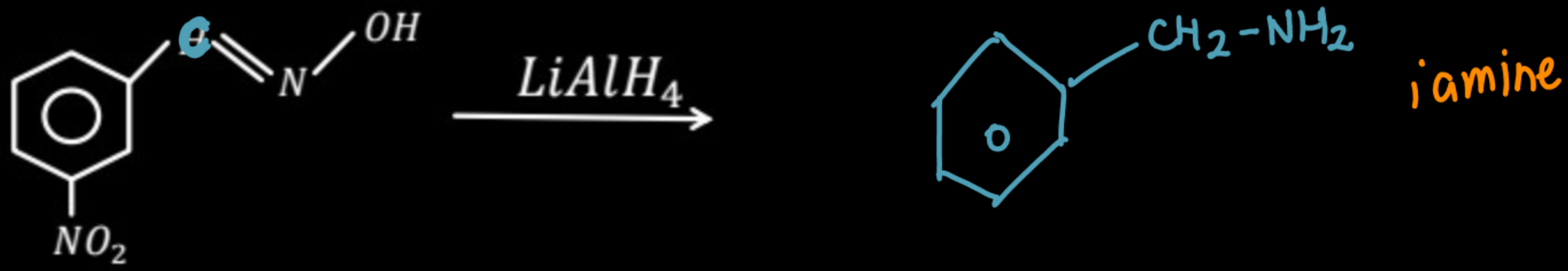


Reduction of oxime

v) Reduction of oxime







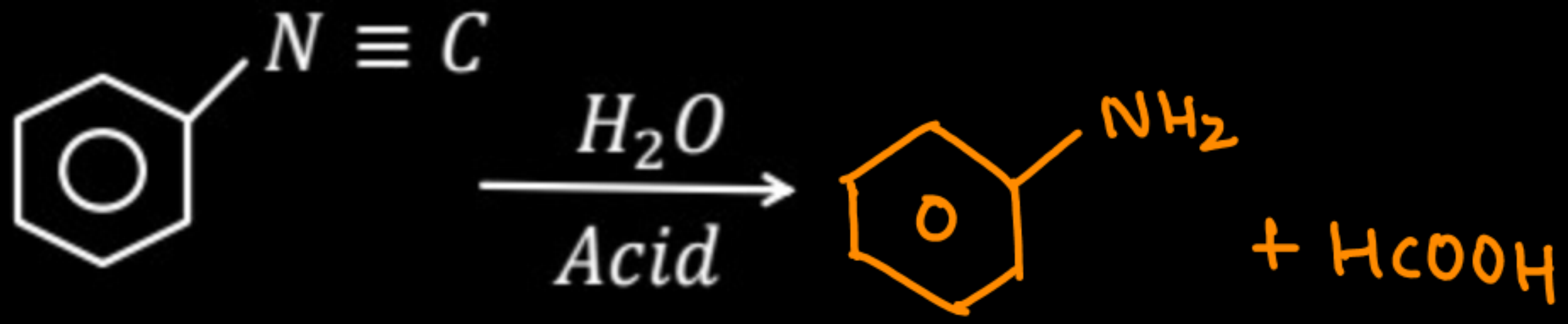
Hydrolysis of isocyanides and isocyanate

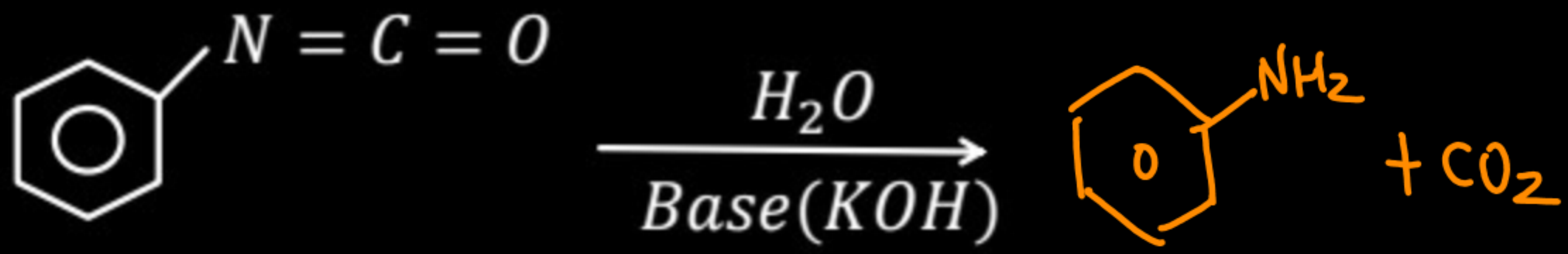
$$R-N\equiv C + H_2O \xrightarrow[\text{Acidic}]{HCl} R-NH_2 + HCOOH$$

Isocyanide

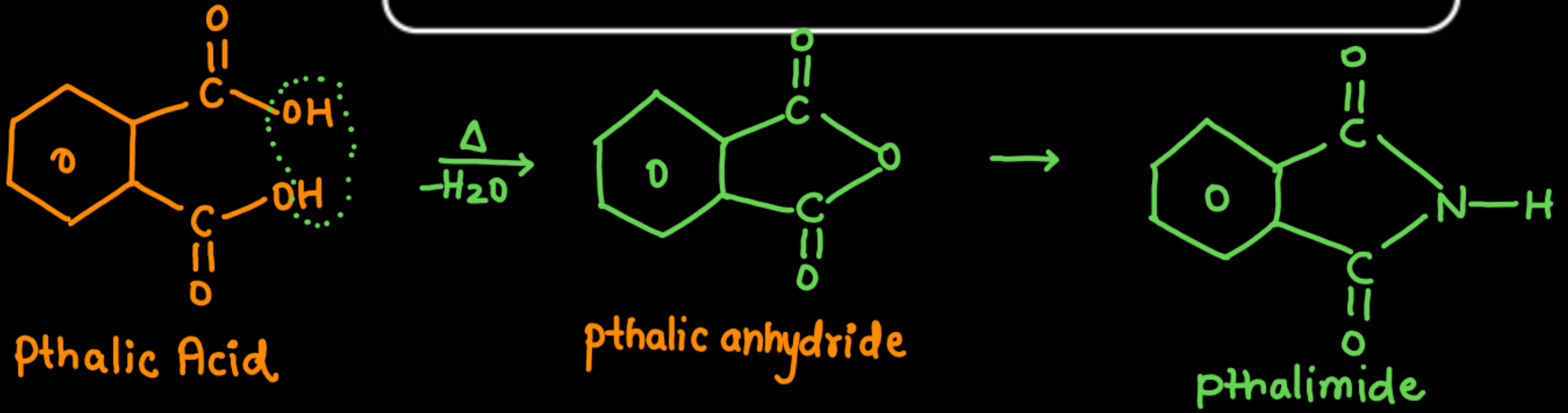
$$R-N=C=O + H_2 \xrightarrow[\text{Basic}]{KOH} R-NH_2 + CO_2$$

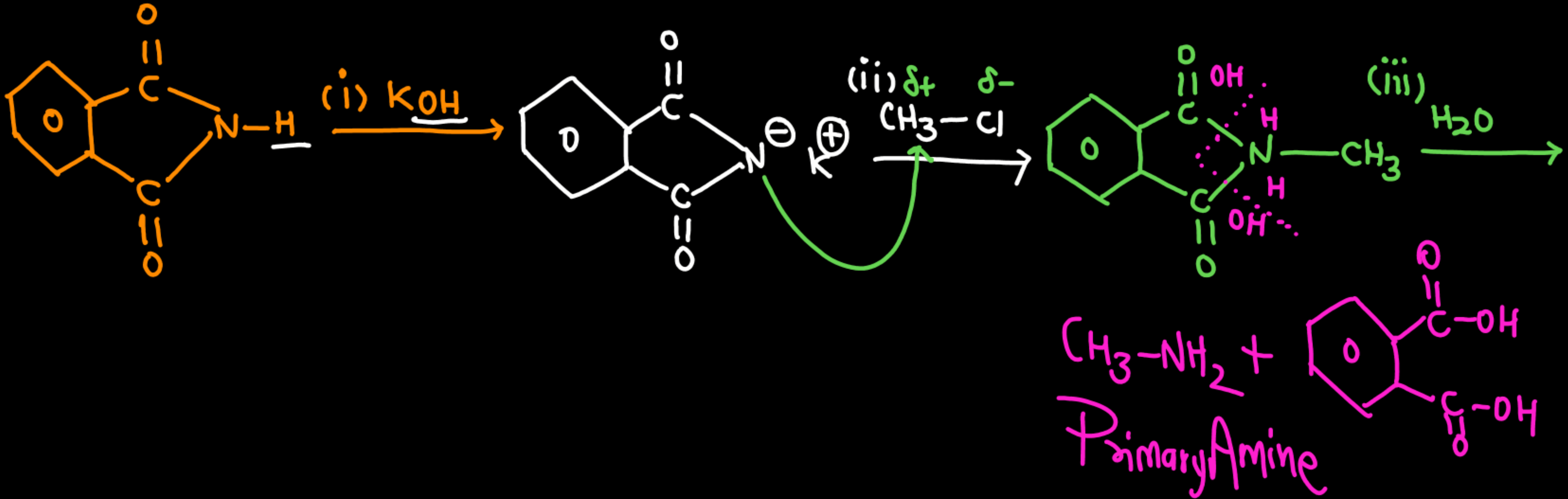
Isocyanate



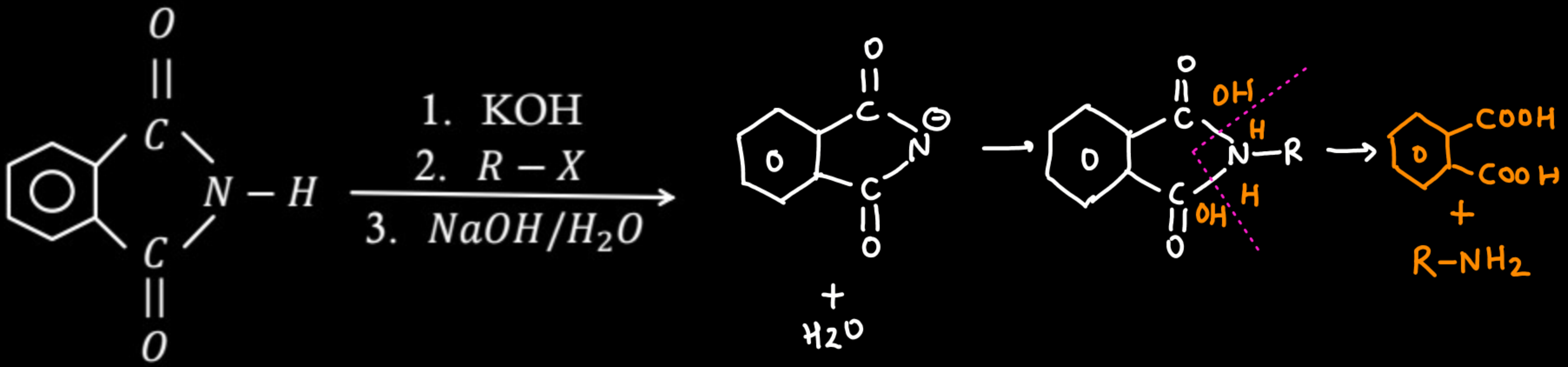


Gabriel phthalimide reaction



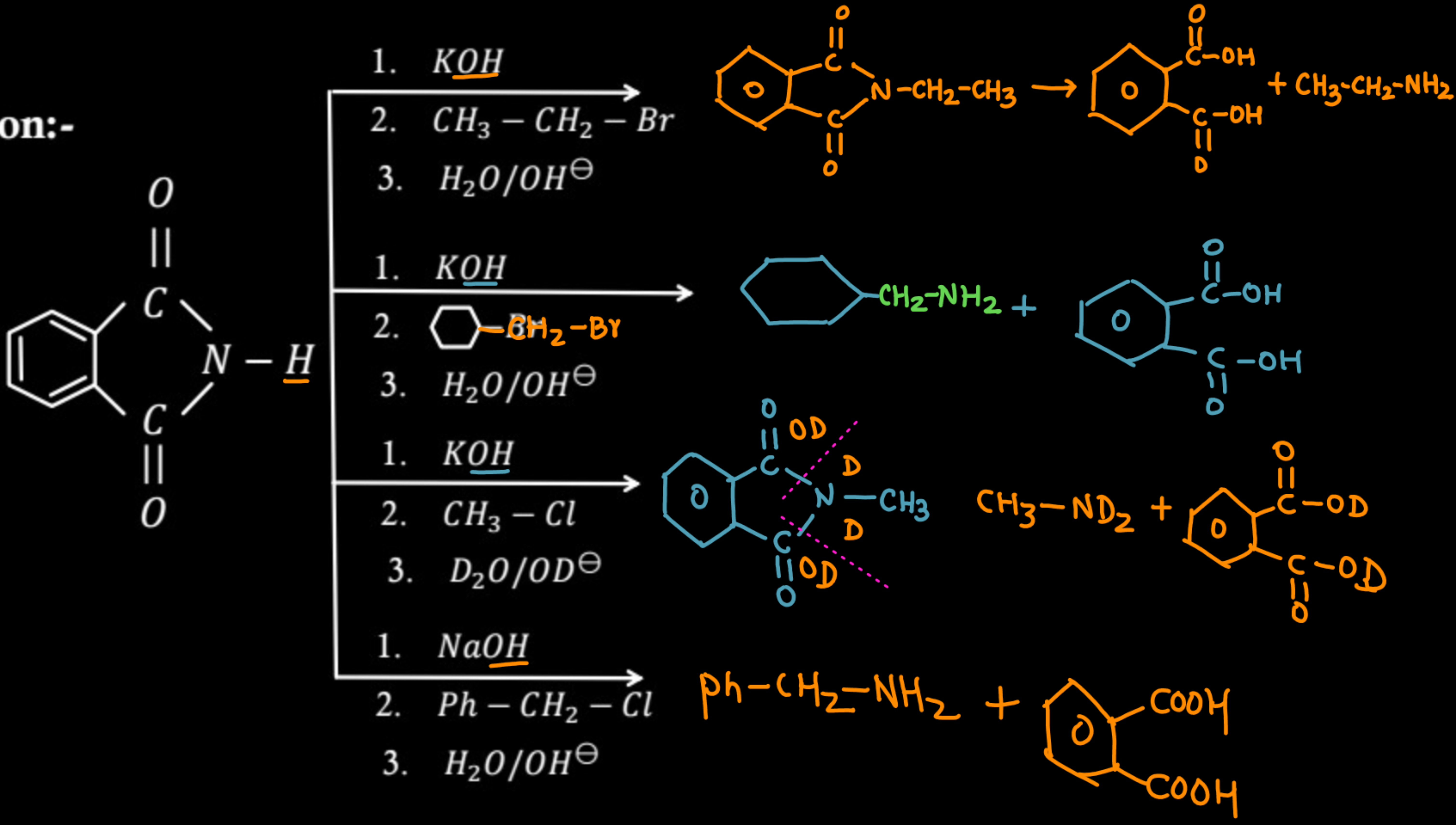


Amines



O
C
N − H
C
O
1. KOH
2. R − X
3. NaOH/H2O
O
C
N
C
O
+
H2O
O
C
OH
H
N−R
C
OH
H
O
COOH
COOH
+
R−NH2

Question:-



1. KOH
2. CH3 – CH2 – Br
3. H2O/OH⊖
N-CH2-CH3
C-OH
+ CH3-CH2-NH2
1. KOH
2. CH2-Br
3. H2O/OH⊖
CH2-NH2 +
C-OH
1. KOH
2. CH3 – Cl
3. D2O/OD⊖
OD
D
N
CH3
CH3-ND2 +
C-OD
1. NaOH
2. Ph – CH2 – Cl
3. H2O/OH⊖
Ph-CH2-NH2 +
COOH

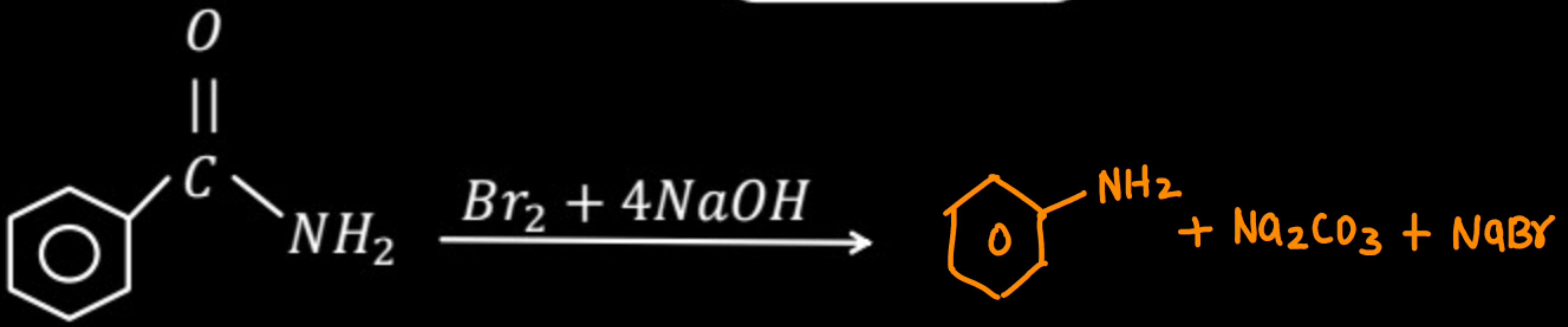


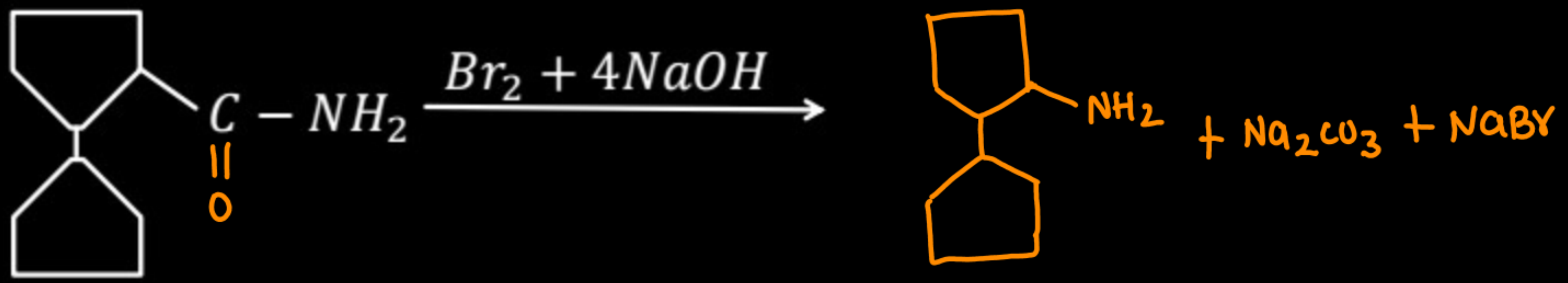
Hoffmann Bromamide degradation

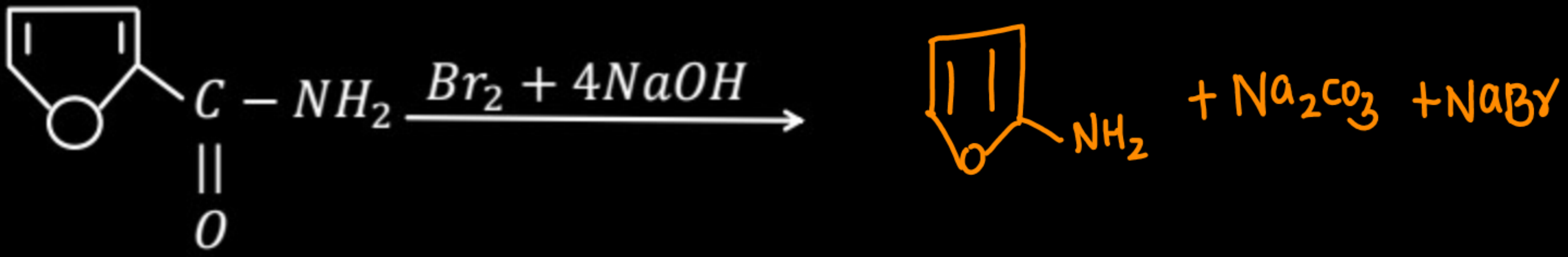
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow{Br_2 + 4NaOH} R-NH_2 + Na_2CO_3 + NaBr$$

Stepdown Reaction

Amines


O
C
NH2
Br2 + 4NaOH
NH2
+ Na2CO3 + NaBr


C − NH2
O
Br2 + 4NaOH
NH2
+ Na2CO3 + NaBr

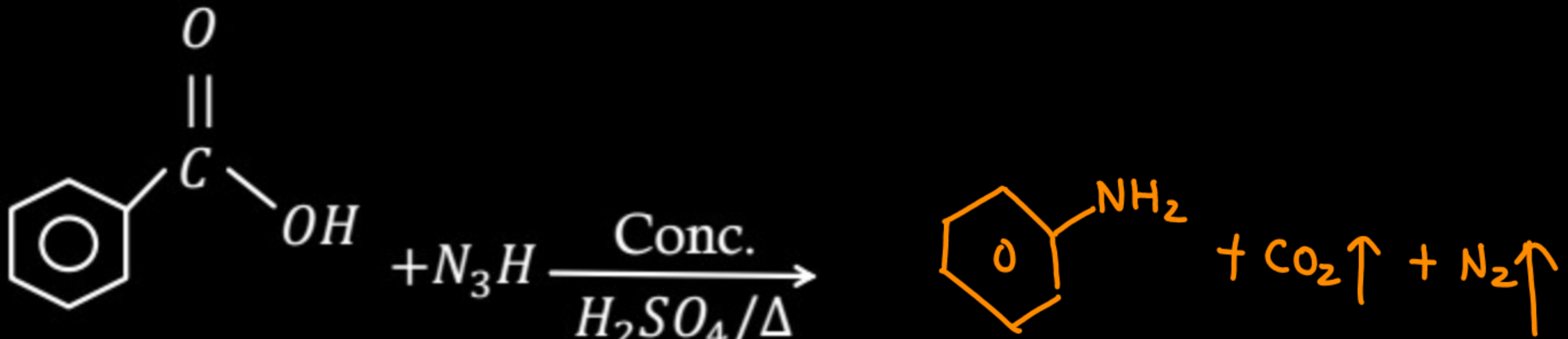

C − NH2
O
Br2 + 4NaOH
NH2
+ Na2CO3 + NaBr

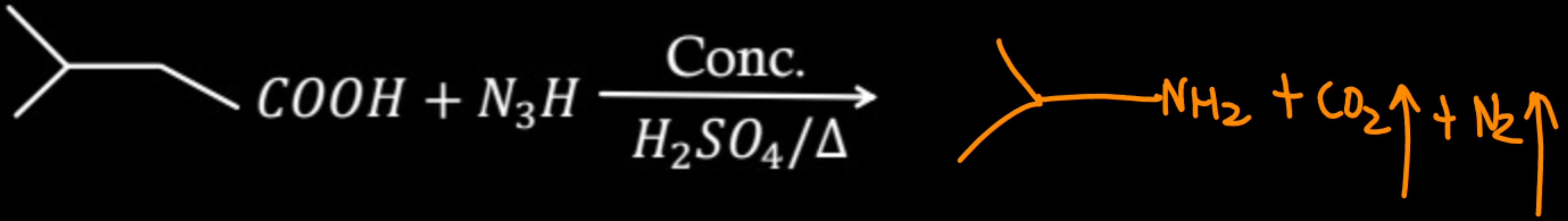
Schmidt Reaction

Sulphuric acid — Carboxylic acid — Hydrazoic acid → N_3H

$$R-\overset{O}{\overset{\|}{C}}-OH + N_3H \xrightarrow[H_2SO_4/\Delta]{\text{Conc.}} R-NH_2 + CO_2\uparrow + N_2\uparrow$$

1°amine







Curtius Reaction

Acid chloride + Sodium azide & Hydrolysis

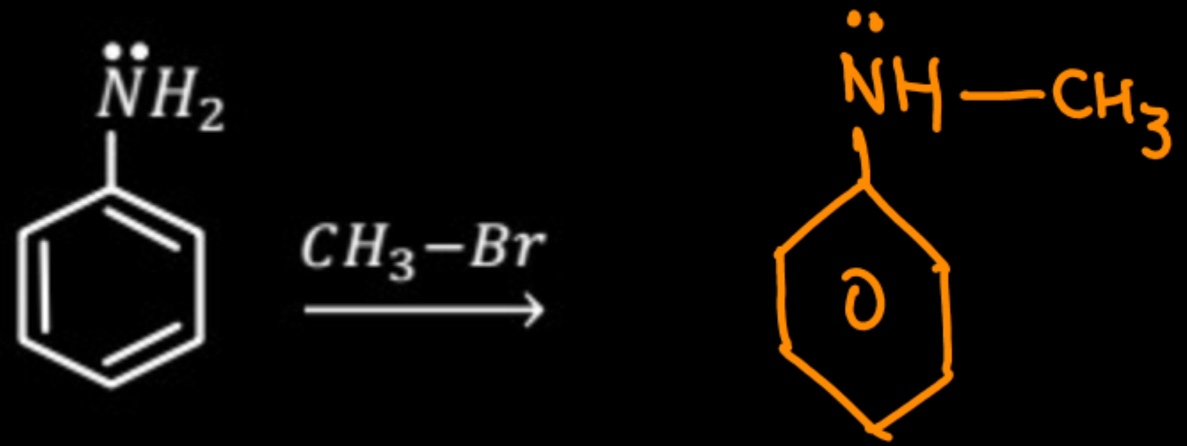
$$R-\overset{\overset{\Large O}{\|}}{C}-Cl \xrightarrow[2.\ H_2O/OH^{\ominus}]{1.\ NaN_3} R-NH_2 + CO_2 + HCl$$

$$Ph-\overset{\overset{\Large O}{\|}}{C}-Cl \xrightarrow[2.\ H_2O/OH^{\ominus}]{1.\ NaN_3} Ph-NH_2 + CO_2 + HCl$$

① Reaction with alkyl halide

$$R-NH_2 \xrightarrow[-HX]{R-X} R-NH-R$$

$$CH_3-NH_2 \xrightarrow[-HCl]{Et-Cl} CH_3-NH-Et$$





Acylation

$$R-NH_2+CH_3-\overset{\overset{O}{\|}}{C}-Cl\xrightarrow{-HCl}R-NH-\overset{\overset{O}{\|}}{C}-CH_3+HCl$$

$$R-NH_2+CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3\xrightarrow{-CH_3OH}R-NH-\overset{\overset{O}{\|}}{C}-CH_3+CH_3-OH$$

$$R-NH_2+CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3\xrightarrow{-CH_3-\overset{\overset{O}{\|}}{C}-OH}CH_3-\overset{\overset{O}{\|}}{C}-OH+R-NH-\overset{\overset{O}{\|}}{C}-CH_3$$

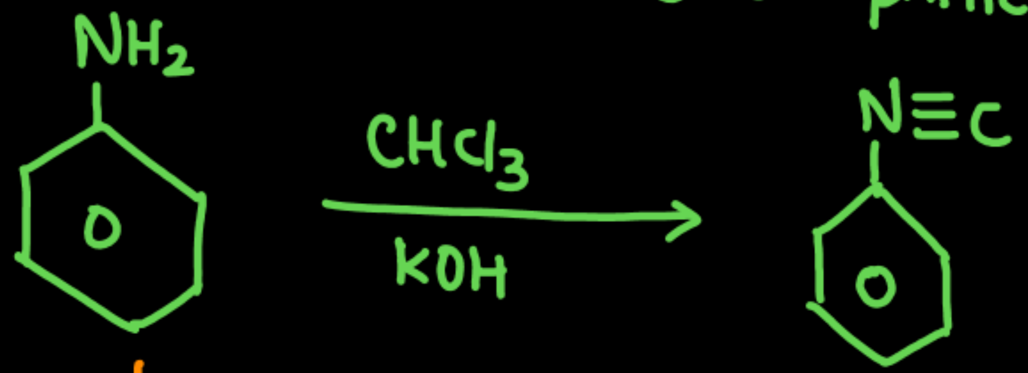


Carbylamines Reaction or isocyanide test

$$R-NH_2 \xrightarrow[KOH]{CHCl_3} R-N\equiv C$$

isocyanide test
or
Carbylamine
(Foul smell)

Intermediate → Carbene
→ $:CCl_2$
→ neutral electrophilic



* 2° amine / 3° amine → donot gives this test.
→ only 1° amine & Aromatic amines gives this test.

Reaction with nitrous acid

HNO_2

1° amine + HNO_2

$R-NH_2 + HNO_2 \longrightarrow$ diazonium salt $R-N_2^+Cl^-$ $\xrightarrow{OH^-}$ $R-OH$

$\xrightarrow{Cl^-}$ $R-Cl$

2° amine + HNO_2

$R_2N-H + HO-N=O \rightarrow R_2N-N=O$

(nitroso comp)

Liberman nitroso test

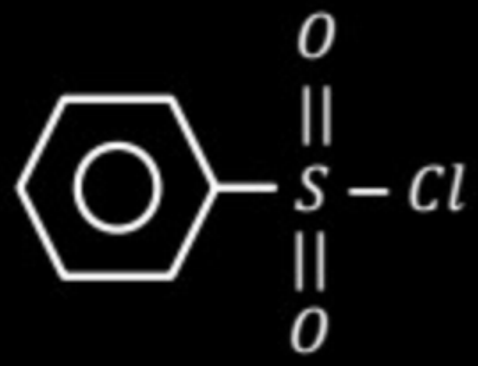
Yellow oily layer

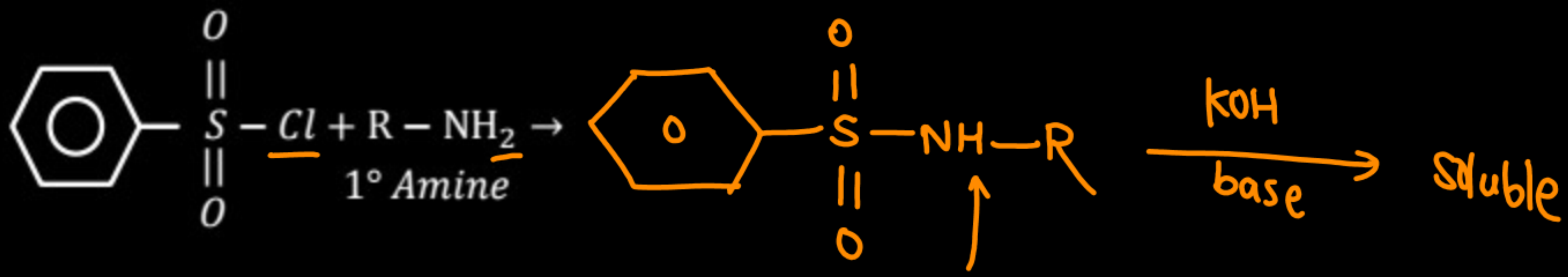
3° amine ✗



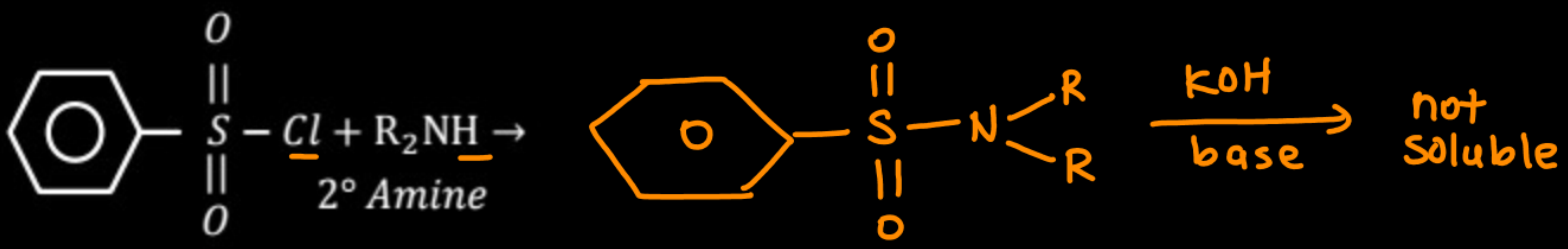
Heinsberg Reagent

Reaction with benzene sulphonyl chloride:-

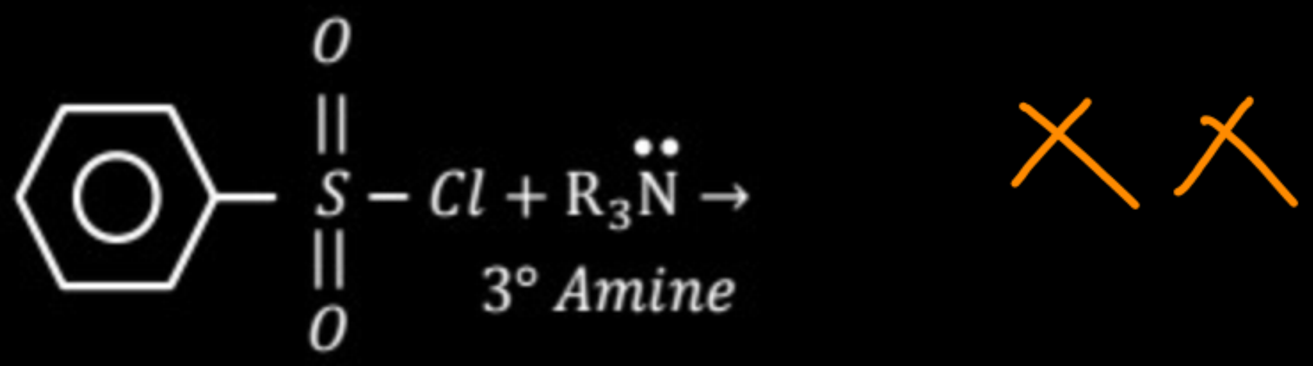




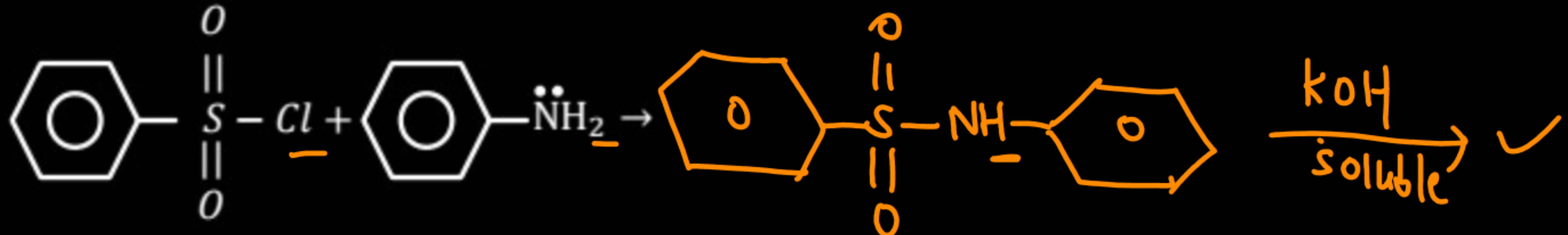
Amines



Cl + R₂NH →
2° Amine
KOH
base
not soluble



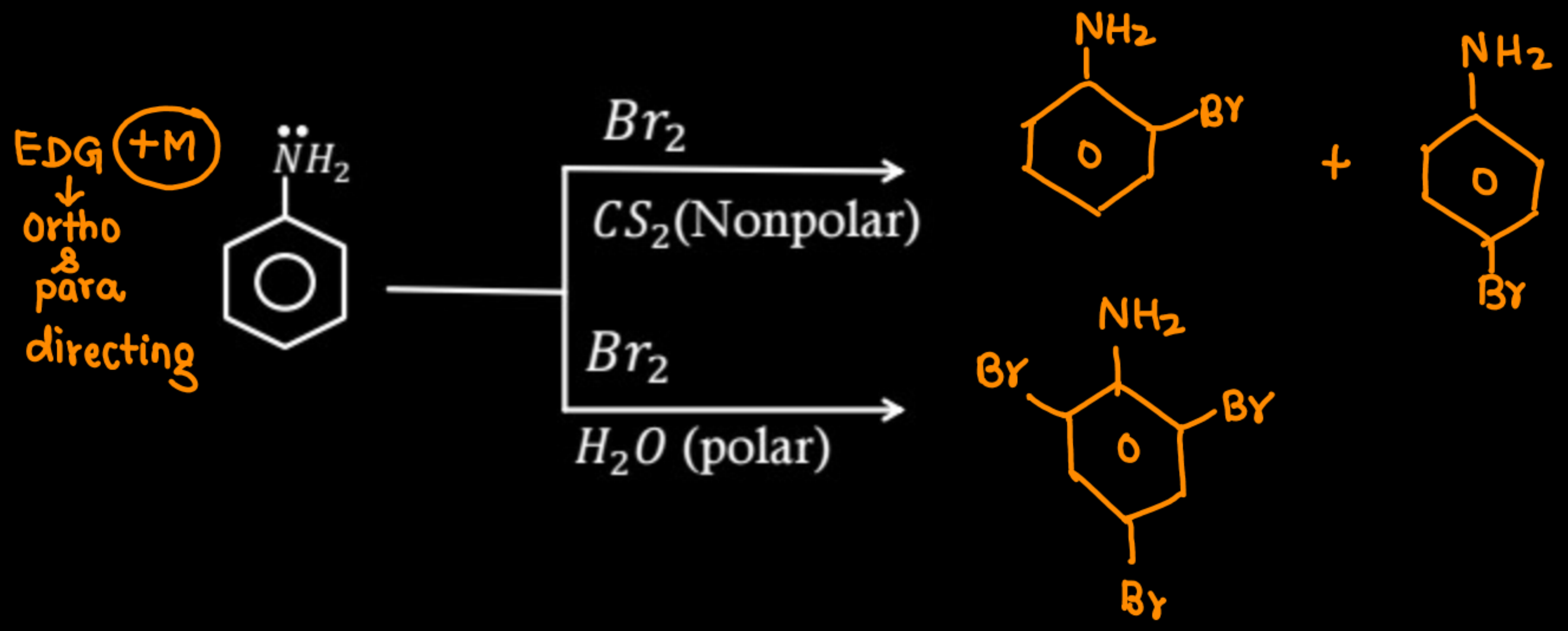
Cl + R₃N̈ →
3° Amine



Cl +
NH₂ →
NH
KOH
soluble

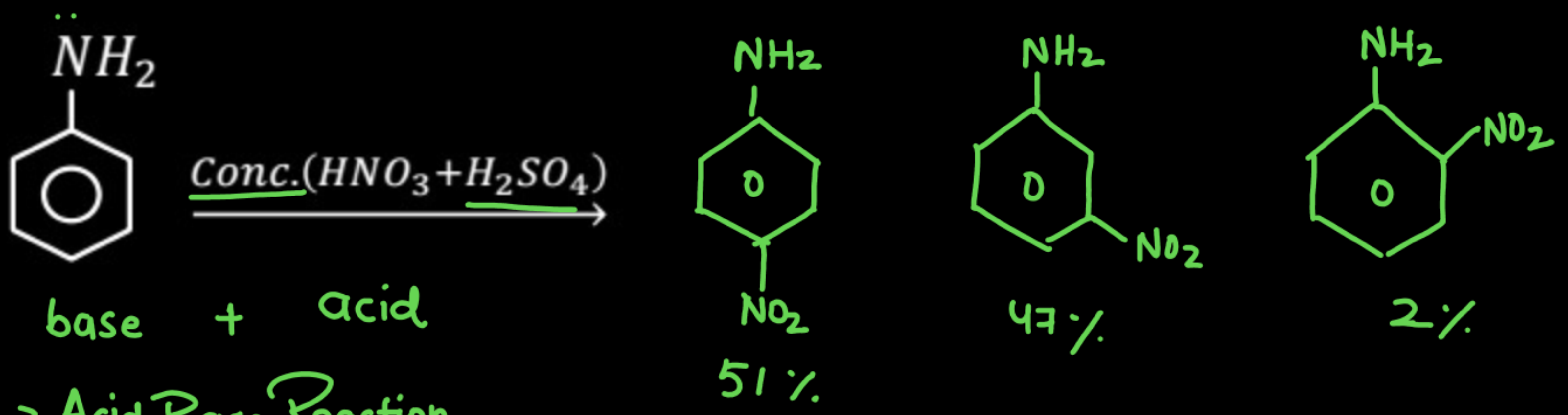
Electrophilic substitution

1. Bromination:-





② Nitration

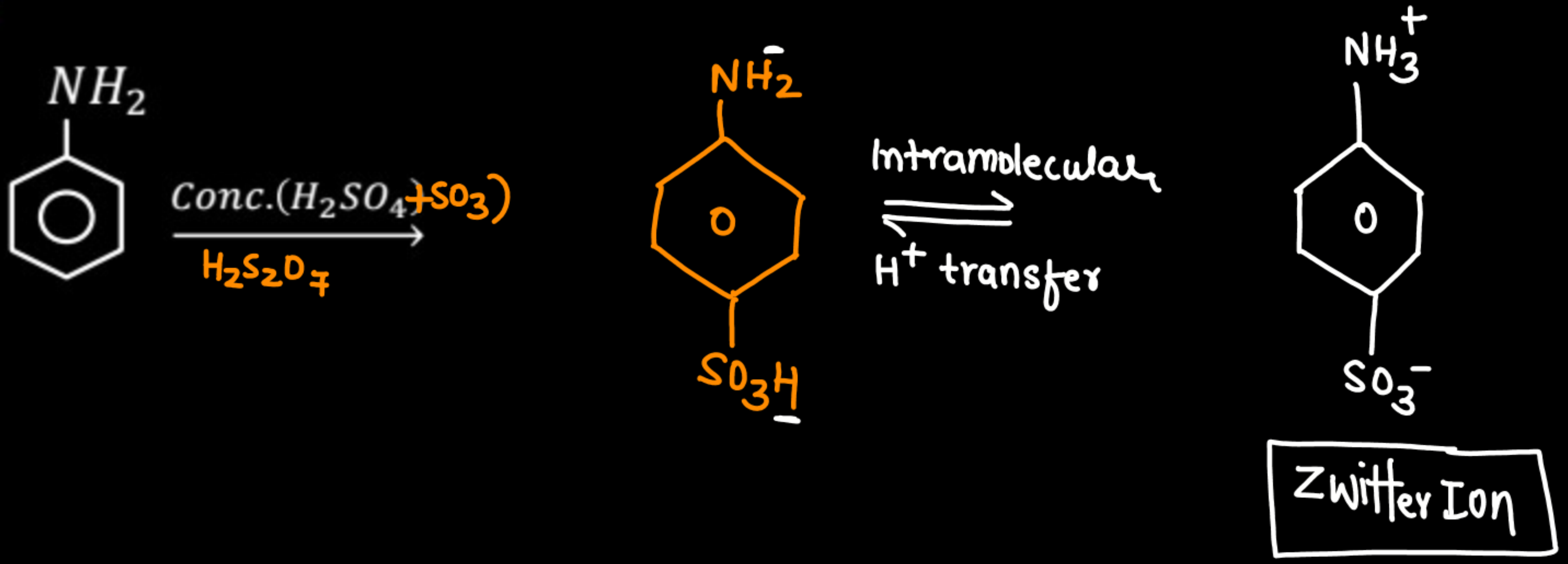


→ Acid Base Reaction

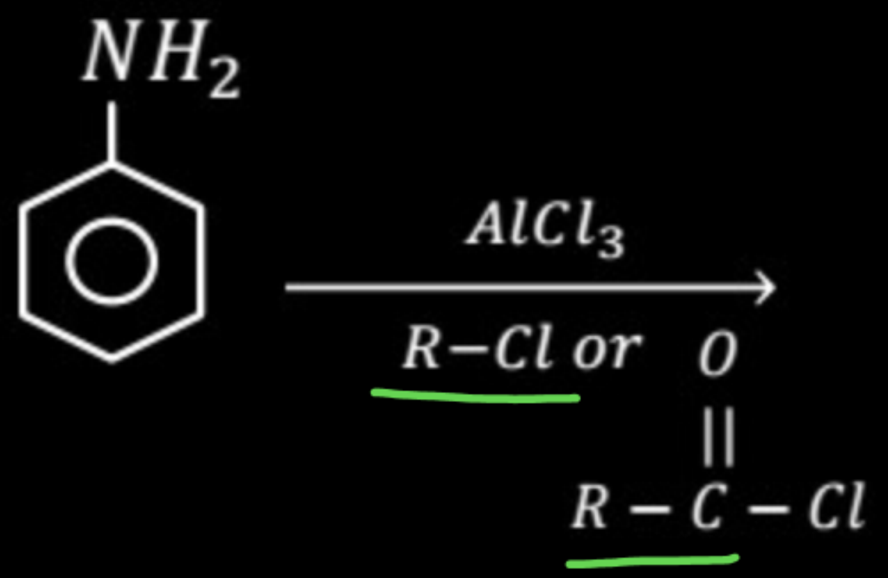


Electron withdrawing → Meta directing

Sulphonation



Friedel craft



no reaction ✗



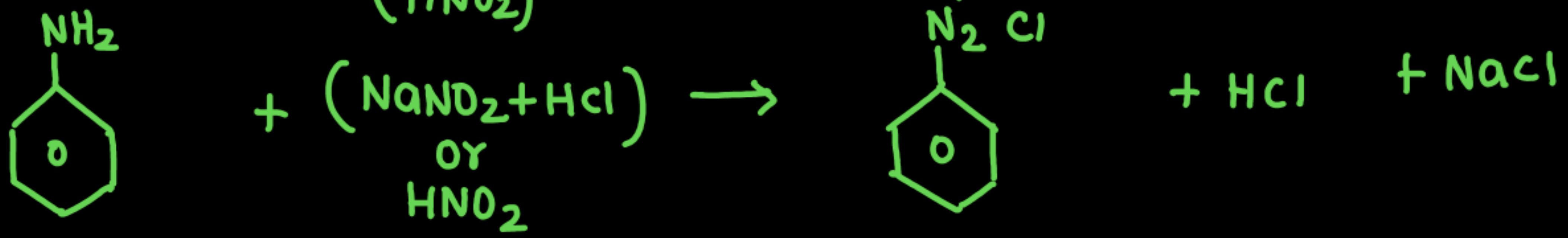
Electron withdrawing



DIAZONIUM SALTS

General formula → $R-\overset{+}{N_2}-\overset{-}{X}$ $\qquad$ $Ph-\overset{+}{N_2}-\overset{-}{X}$

$$CH_3-NH_2 + (NaNO_2 + HCl) \text{ or } (HNO_2) \longrightarrow CH_3-\overset{+}{N_2}\overset{-}{Cl} + HCl + NaCl$$



$$Ar\overset{\oplus}{N_2}X^{\ominus} \xrightarrow{Cu_2Cl_2/HCl} Ar-Cl + N_2\uparrow$$

$$Ar\overset{\oplus}{N_2}X^{\ominus} \xrightarrow{Cu_2Br_2/HBr} Ar-Br + N_2\uparrow$$

$$Ar\overset{\oplus}{N_2}X^{\ominus} \xrightarrow{CuCN/KCN} Ar-CN + N_2\uparrow$$

Sandmeyer Reaction

Amines



2. Replacement by iodide ion:-

$$Ar\overset{+}{N}_2Cl^- + \underline{KI} \rightarrow Ar{-}I + N_2\uparrow$$



Amines

3. Replacement by Fluoride ion:-

$$Ar\overset{+}{N}_2Cl^- + HBf_4 \rightarrow Ar{-}F + N_2\uparrow$$

Fluoroboric acid

4. Replacement by H:-

$$Ar\overset{+}{N}_2Cl^- + H_3PO_2 + H_2O \rightarrow Ar-H$$

Hypo phosphorous Acid

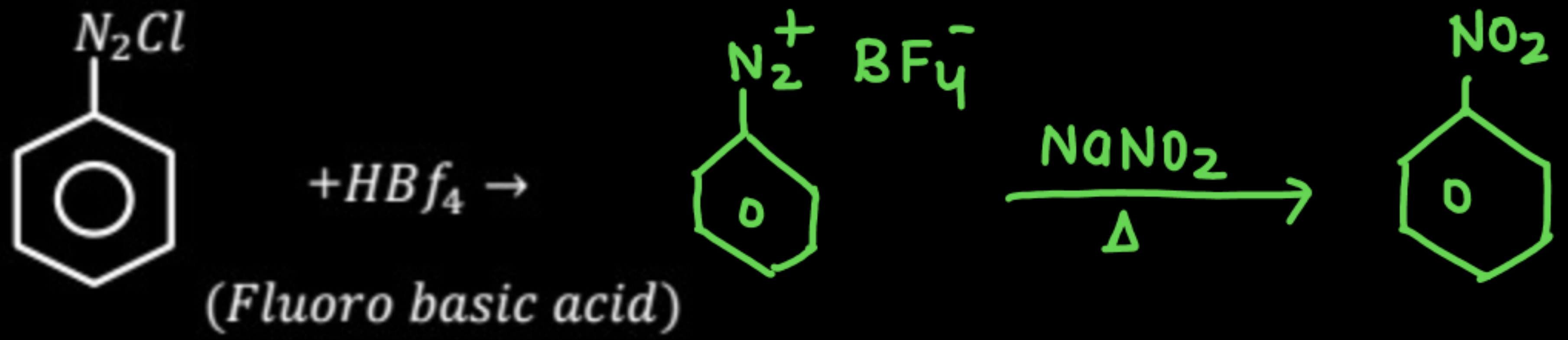
Or phosphinic acid

5. Replacement by Hydroxyl group:-

$$ArN_2Cl + H_2O \xrightarrow{upto\ 283\ K} Ar—OH$$

Amines

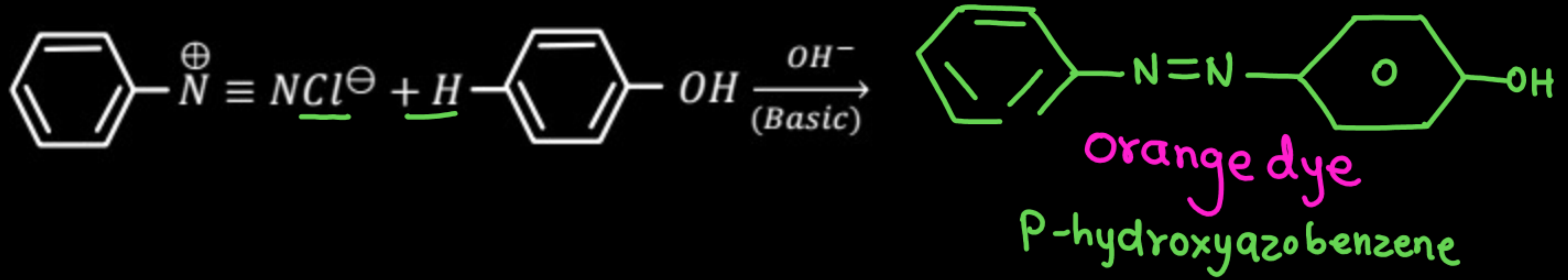
6. Replacement by NO_2 group:-

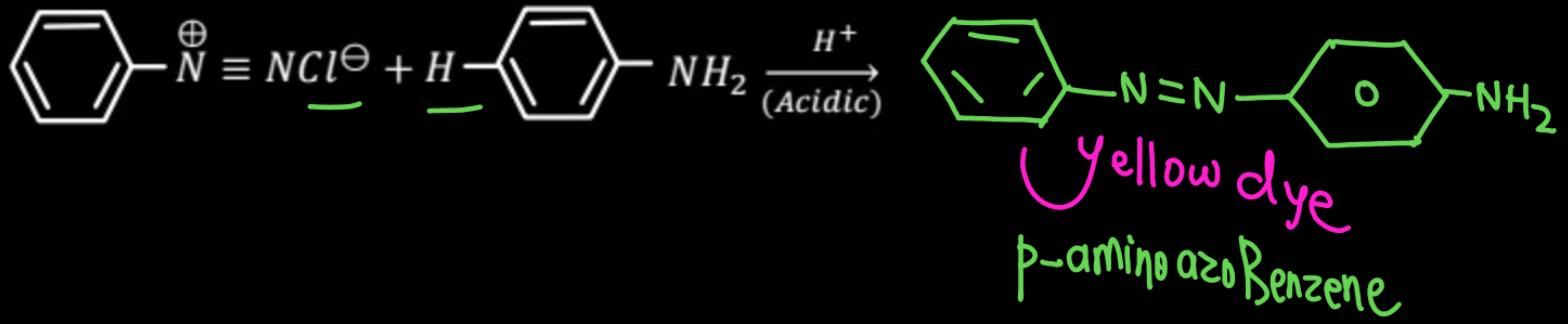


Amines

Dye

B. Reaction involving retention of diazo group :-





THANK YOU

All the Best!!

Method of Purification of Organic Comp

Practical organic Chemistry

PRACTICAL ORGANIC CHEMISTRY

(A) FUNCTIONAL GROUP ANALYSIS

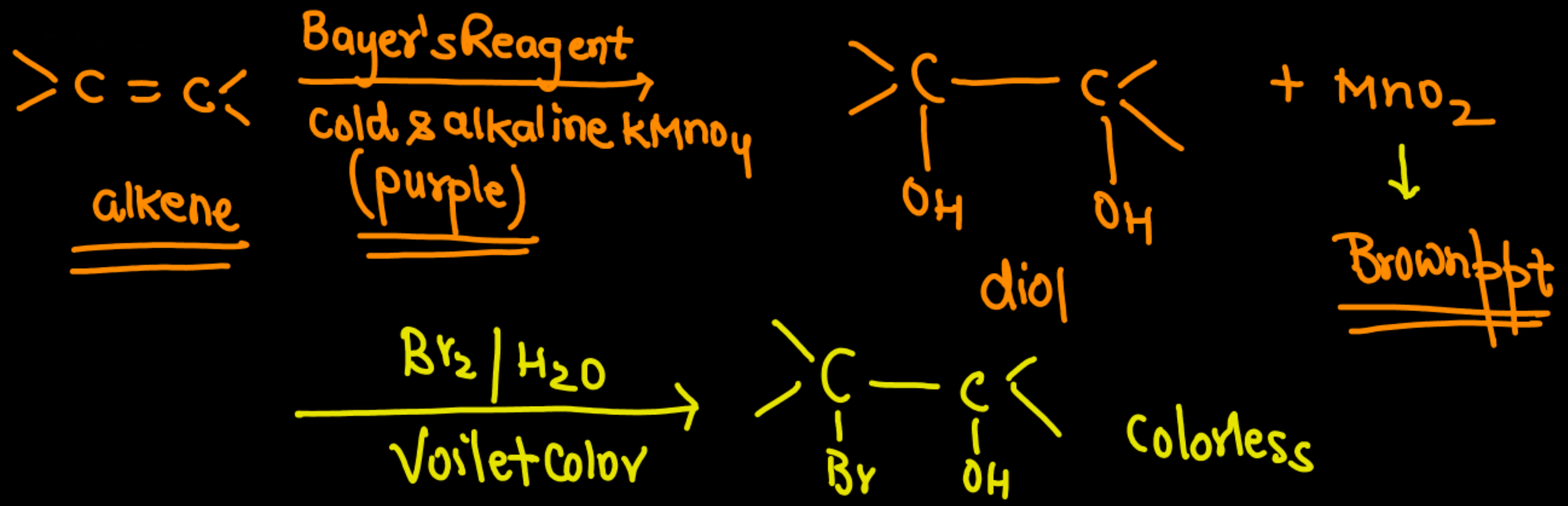
1. **Unsaturation : Alkenes & alkynes:**

(a) Bayers test : Cold dil alk. $KMnO_4$ decolourisation test

Purple colour → Colourless + MnO_2 (Brown ppt)

(b) Br_2 water decolourisation test

Violet colourless of Br_2 → Colourless



2. ***Terminal alkynes:***

Confirmed by ppt of Acetylide ion with $NaNH_2$ or $AgNO_3$ or $Cu_2Cl_2 + NH_4OH$

3. ***Alkyl halides:***

(a) If they are capable of carbocation formation then they will give ppt with $AgNO_3$.

$R-Cl$, $R-Br$, $R-I$ $+ AgNO_3 \rightarrow$

$AgCl$ white color.

$AgBr$ Light yellow color.

AgI Dark yellow color.

$$CH_3-C\equiv C-H + NaNH_2 \longrightarrow CH_3-C\equiv C^{\ominus}\ Na^{\oplus} + NH_3$$

Terminal alkyne

acidic H

Sodium acetylide

Ppt formation

$$+ Cu_2Cl_2 + NH_4OH \longrightarrow CH_3-C\equiv C^{\ominus}\ Cu^{\oplus} + NH_3 + HCl$$

Copper acetylide

Ppt formation

Alcohol + CAN → Red color

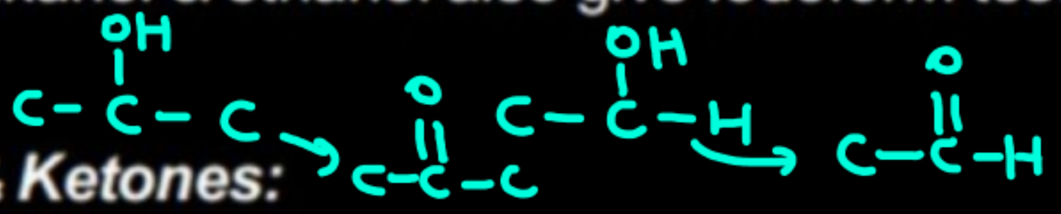
Alcohol + acetic acid + conc H_2SO_4 $\xrightarrow{\Delta}$ Fruity smell

4. ***Alcohol:*** CAN Test

(a) Cerric ammonium nitrate → Give red colour

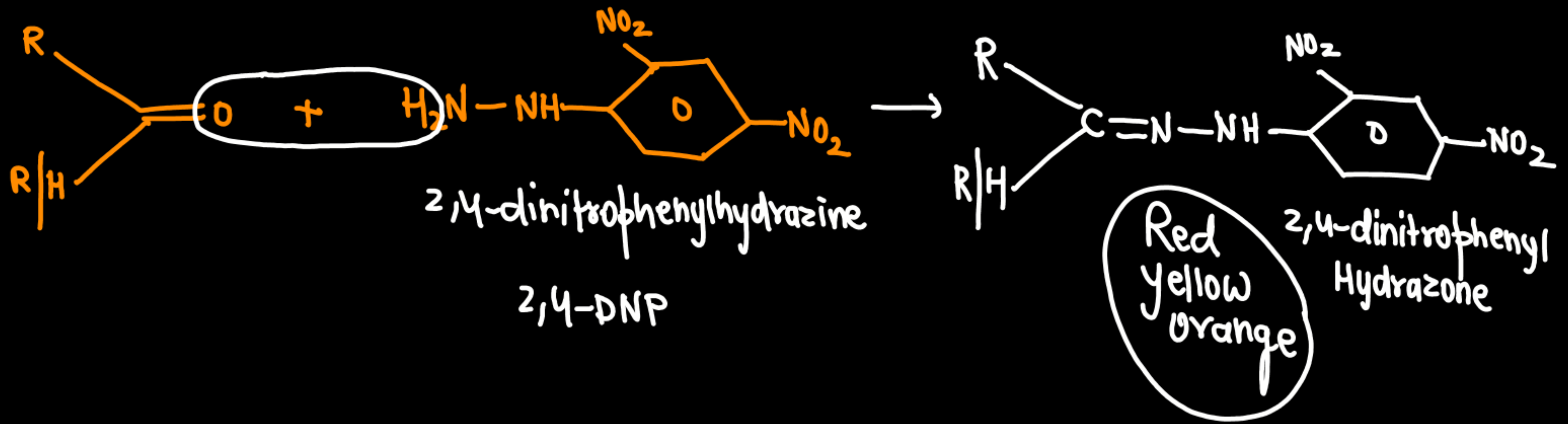
(b) Boil with acetic acid & conc. H_2SO_4 → fruity smell

(c) 2-alkanol & ethanol also give Iodoform test → Yellow ppt. of CHI_3 on reaction with $I_2 + \overset{\ominus}{O}H$



5. ***Aldehyde & Ketones:***

2,4- Dinitrophenyl hydrazine (2,4-DNP) (or) Braddy's reagent give yellow, orange or red color with ald. & Ketones



6. ***Aldehydes:*** $[Ag(NH_3)_2]^+$

(a) Tollen's test → Silver mirror (aliphatic + aromatic)

(b) Fehling's test {except benzaldehyde}→ Red colour (only aliphatic)
Red Brown ppt (Cu_2O)

(c) Benedicts test → Red colour
Cu_2O Red brown ppt

(d) Schiff's dye colour regeneration test → Pink colour

(e) Gly ppt with $HgCl_2$. white ppt

7. ***Ketones:***

(a) Methyl Ketones give haloform test

(b) α-hydroxy Ketones give Tollen's & Fehling test's too.

8. *Carboxylic acids:*

(a) Brisk effervescence with aq. $NaHCO_3$ solution.

(b) HCOOH alone gives silver mirror test with Tollen's reagent. & Fehling soln Test

(c) Blue litmus → red

(d) Give fruity smell on reaction with alcohols.

9. *Phenols:*

(a) Violet colouration with neutral $FeCl_3$

(b) Liebermann test

(c) White ppt with Br_2 water

(d) Brisk effervescence with aq. $NaHCO_3$ is observed in case of Nitrophenols.

10. **Primary amines:**

discussed in last chapter

(a) Carbylamine reaction → Isonitriles have very distinctive foul odors

(b) Hoffmann mustard oil reaction → Oily liquid with mustard like smell.

11. Aromatic 1° amine → diazo test

12. Amide boil with NaOH → NH_3

14. ***Proteins:***

(a) Biuret test : Also used for urea → Alkaline solution of protein treated with a drop of aq $CuSO_4$ when bluish violet colour is obtained

(b) Ninhydrin test : Protein treated with a pyridine solution of ninhydrin give colour ranging from deep blue to violet pink.

15. **Carbohydrate :**

Molish test → Glucose + conc. H_2SO_4 + α nephthol → violet colour.

DIFFERENTIATION TEST

D1. ***1°, 2° & 3° alcohols:***

(a) Lucas test : Lucas reagent is conc. HCl + $ZnCl_2$

3° alcohol → immediate ppt
2° alcohol → 5 min ppt
1° alcohol → 30 min ppt

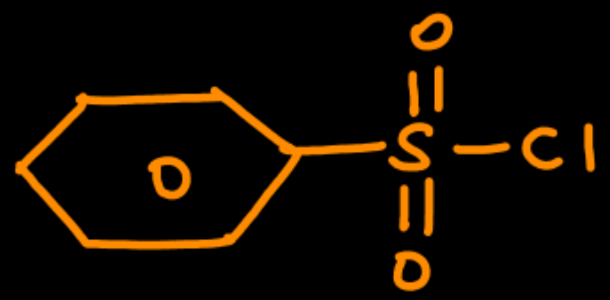
(b) Victor Meyer's test (RBC test)

(i) 1° Alcohol → Blood red colour

(ii) 2° Alcohol → Blue

(iii) 3° Alcohol → Colourless

D2. ***1°, 2° & 3° amines:***



Hinsberg's reagent :

(i) 1° Amine yield a clear solution from which upon acidification an insoluble material separated.

(ii) 2° Amine yield an insoluble compound which is unaffected by acid

(iii) 3° Amine yield insoluble compound

(B) ELEMENTAL ANALYSIS

Lassaigne method (Detection of elements)

Element	Sodium Extract (S.E.)	Confirmed Test	Reactions
Nitrogen	$Na + C + N \xrightarrow{\Delta} NaCN$ (S.E.)	S..E.+ $FeSO_4$ + NaOH, boil and cool, + $FeCl_3$ + conc. HCl Blue or green colour	$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$ $Fe(OH)_2 + 6NaOH \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$ $Na_4[Fe(CN)_6] + FeCl_3 \xrightarrow{HCl} Fe_4[Fe(CN)_6]_3 + 3NaCl$ Pr ussian blue
Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$ (S.E.)	(i) S.E. + sodium nitro prusside (A) A deep violet colour. (ii) S.E. + CH_3COOH + $(CH_3COO)_2Pb$ A black ppt.	(i) $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$ (A) deep violet (ii) $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} PbS\downarrow + 2CH_3COONa$ black ppt.
Ha log en	$Na + Cl \xrightarrow{\Delta} NaCl$ (S.E.)	S.E. + HNO_3 + $AgNO_3$ (i) White ppt. so lub le in aq NH_3 confirms Cl (ii) Yellow ppt partially so lub le in aq. NH_3 confirm Br (iii) Yellow ppt inso lub le in aq NH_3 confirms I	$NaX + AgNO_3 \xrightarrow{HNO_3} AgX\downarrow$ ppt $AgCl + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]Cl$ white ppt so lub le
Nitrogen and Sulphur together	$Na + C + N + S \xrightarrow{\Delta} NaCNS$ (S.E.)	As in test for nitrogen; instead of green or blue colour, blood red coloration confirms presence of N and S both	$NaCNS + FeCl_3 \longrightarrow [Fe(CNS)]Cl_2 + NaCl$ blood red colour

(amount of nitrogen)

ESTEMATION OF NITROGEN IN ORGANIC COMPOUND:-

1. Dumas Method   2. Kjeldahls Method

1. Dumas Method:

The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of CO_2, yields free nitrogen in addition to carbon dioxide and H_2O

$$C_xH_yN_z + \left(2x + \frac{y}{2}\right) CuO \xrightarrow{\Delta} xCO_2 + \frac{y}{2} H_2O + \frac{z}{2} N_2 + \left(2x + \frac{y}{2}\right) Cu$$

nitrogen containing organic comp

copper oxide

further Heating with copper

↑ amt of nitrogen ??

⇓ passed through aq KOH

⇓ CO_2 absorbed

N_2 gas remains in sol^n

~~6 - 8~~ ← 8.00 am

4 - 6

7 - 9

10 - 12

12 - 2

- Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gases. The mixture of gases so produced is collected over aq solution KOH which absorbs CO_2. Nitrogen is collected in the upper part of the graduated tube.

Let mass of organic compound = m gm

Volume of nitrogen colected = V_1 ml

Room temp. = T_1K

$$\text{Volume of Nitrogen at STP} = \frac{P_1V_1 \times 273}{760 \times T_1}$$

Where P_1 & V_1 are the pressure and volume of nitrogen.

P_1 is different from the atmospheric pressure at which nitrogen gas is collected.

The value of P_1 is obtained by the relation P_1 = Atmospheric pressure – aqueous tension

22400 ml N_2 at STP weighs 28g

$$\text{V ml } N_2 \text{ weighs (at STP)} = \frac{28V}{22400}\text{g} \quad ; \quad \text{\% of N} = \frac{28V \times 100}{22400 \times m}$$

2. Kjeldahl's Method:

- The compound containing nitrogen is heated with concentrated sulphure acid. Nitrogen in the compound gets converted to ammonium sulphate.
- The resulting acid mixture is then heated with excess sodium hyddroxide. The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid.
- The amount of ammona produced is determined by estimating the amount of sulphuric and consumed in the reaction. It is done by estimating unreated sulphure acid left after absorption of ammonia by titrating it with standerd alkali solution.
- The difference b/w the net amount of acid taken and that left after the reaction gives the amount of acid heacted with ammonia.

NH_4^+ SO_4^{-2} Na^+ OH^-

$$\text{Organic comp.} + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

liberated ammonia gas
+
Conc H_2SO_4

(known moles of H_2SO_4)

Let mass of organic compd taken = m gm

Volume of H_2SO_4 of molarity M = V ml

Volume of NaOH of molarity M used for titration of excess of H_2SO_4 = V_1 ml

V_1 ml of NaOH(M) = $\frac{V_1}{2}$ ml of H_2SO_4(M) ; Volume of H_2SO_4(M) unused = $\left(V - \frac{V_1}{2}\right)$ ml

$\left(V - \frac{V_1}{2}\right)$ ml H_2SO_4(M) = $2\left(V - \frac{V_1}{2}\right)$ ml of NH_3(M)

1000 ml of 1M NH_3 solution contains 17gm NH_3 or 14 gm N

$\therefore$ $2(V-V_1/2)$ ml of NH_3 contains = $\frac{14 \times M \times 2(V - V_1/2)}{1000}$ gm of N

$$\% \text{ of Nitrogen} = \frac{14M \times 2\left(V - \frac{V_1}{2}\right)}{1000 \times m} \times 100 \quad = \frac{1.4M \times 2\left(V - \frac{V_1}{2}\right)}{m}$$

- Kjeldahl method is not applicable to compounds containing Nitrogen in Nitro & Azo group and Nitrogen present in the ring as nitrgen of these compounds does not change to amonium sulphate under these condition.
- **Carius method:** known mass of an organic compd is heated with fuming nitric acid in pressere of silver nitrated contained in hard glass tube known as carius tube.

Organic comp + Fuming HNO_3 →



Carius tube

$AgNO_3$ (silver nitrate lining in glass tube)

BIOMOLECULES

Carbohydrates

Biomolecule — 80% weightage Carbohydrate.

t.me/VTSIR1

Old def: $C_x(H_2O)_y \rightarrow$ Carbohydrate

eg. $C_6H_{12}O_6 \rightarrow C_6(H_2O)_6$

$C_{12}H_{22}O_{11} \rightarrow C_{12}(H_2O)_{11}$ } Carbohydrate

$CH_3COOH \rightarrow C_2(H_2O)_2$ } not Carbohydrate

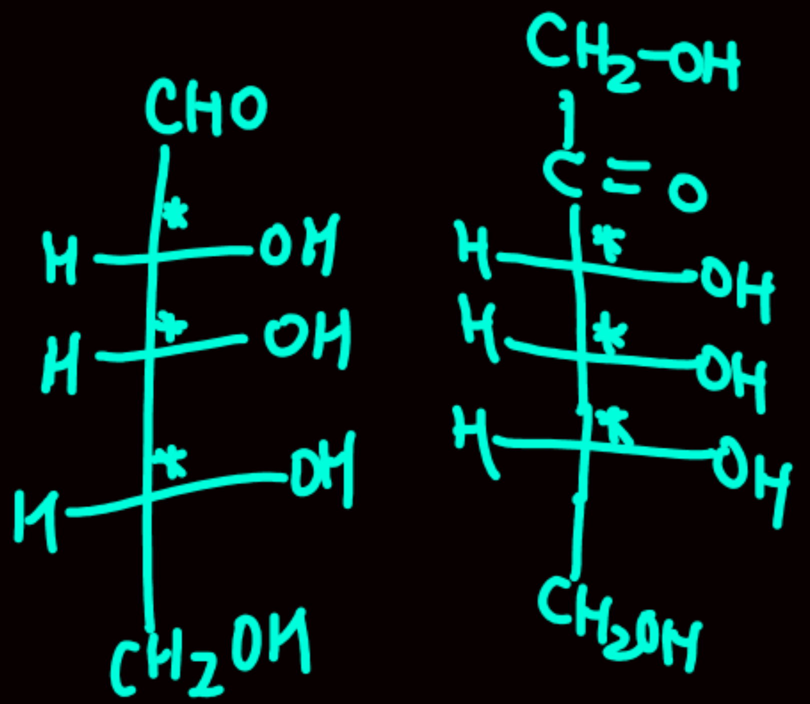
Acetic acid

$C_6H_{12}O_5 \rightarrow \times$ } Carbohydrate

Rhamnose

New def:

* optically active compound, which contains polyhydroxy aldehyde or poly hydroxy ketone are called Carbohydrates.
* comp which produces poly Hydroxy aldehyde/ketone on Hydrolysis are called Carbohydrate.



→ Carbohydrates are also k/a Saccharides.

→ Carbohydrates which are sweet in taste are called Sugar.

(Classification) Types of Carbohydrates.

① polysaccharides
↓ H_3O^+
produces Hundreds molecules of Saccharides.

② Oligosaccharides
↓ H_3O^+
produces 2-10 molecule of Saccharides

③ MonoSaccharides.
↓ H_3O^+
✗
(Basic unit of Carbohydrate)

* Saccharides Containing aldehyde group ⟶ Aldose
" " Ketone " ⟶ ketose

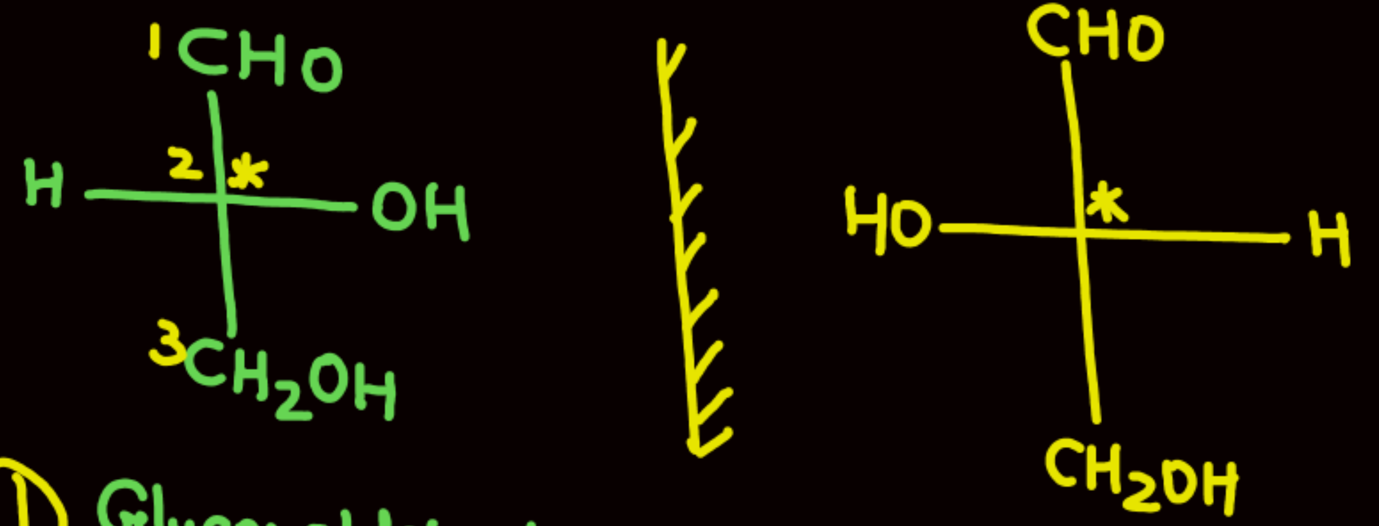
(ose)

OTSE

Monosaccharides

① Aldotriose

- Ald → aldehyde group
- tri → 3 carbon
- ose → saccharides (carbohydrates)

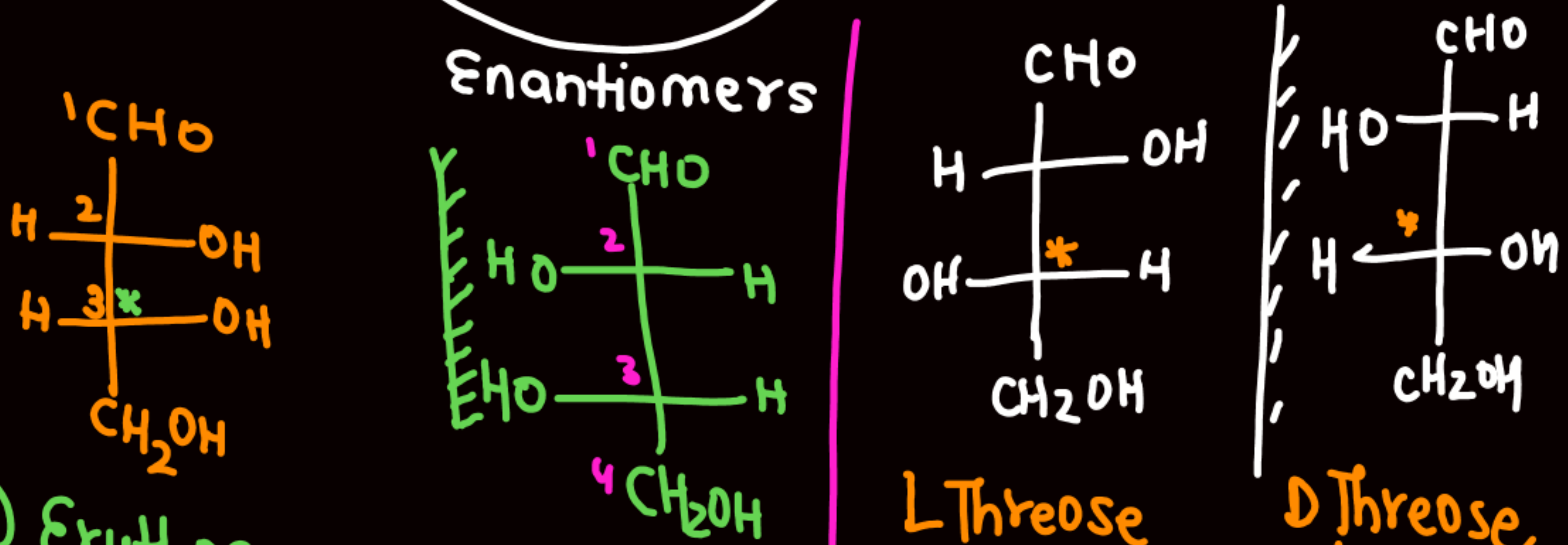


D Glyceraldehyde   L Glyceraldehyde

Enantiomers

② Aldotetrose

- Ald → aldehyde
- tetr → 4 carbon
- ose → saccharides (carbohydrates)



D Erythose   L Erythrose

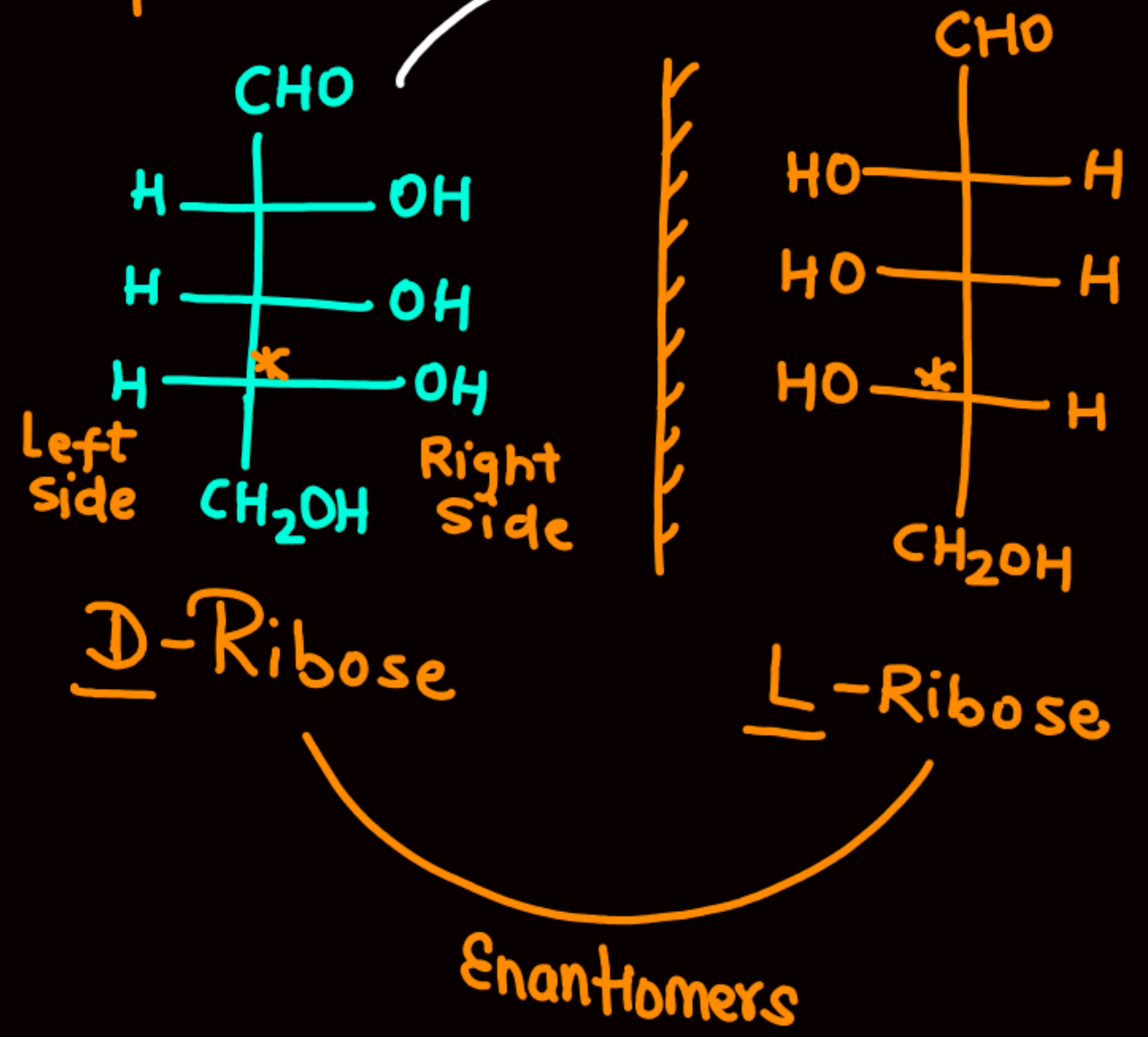
Enantiomer.

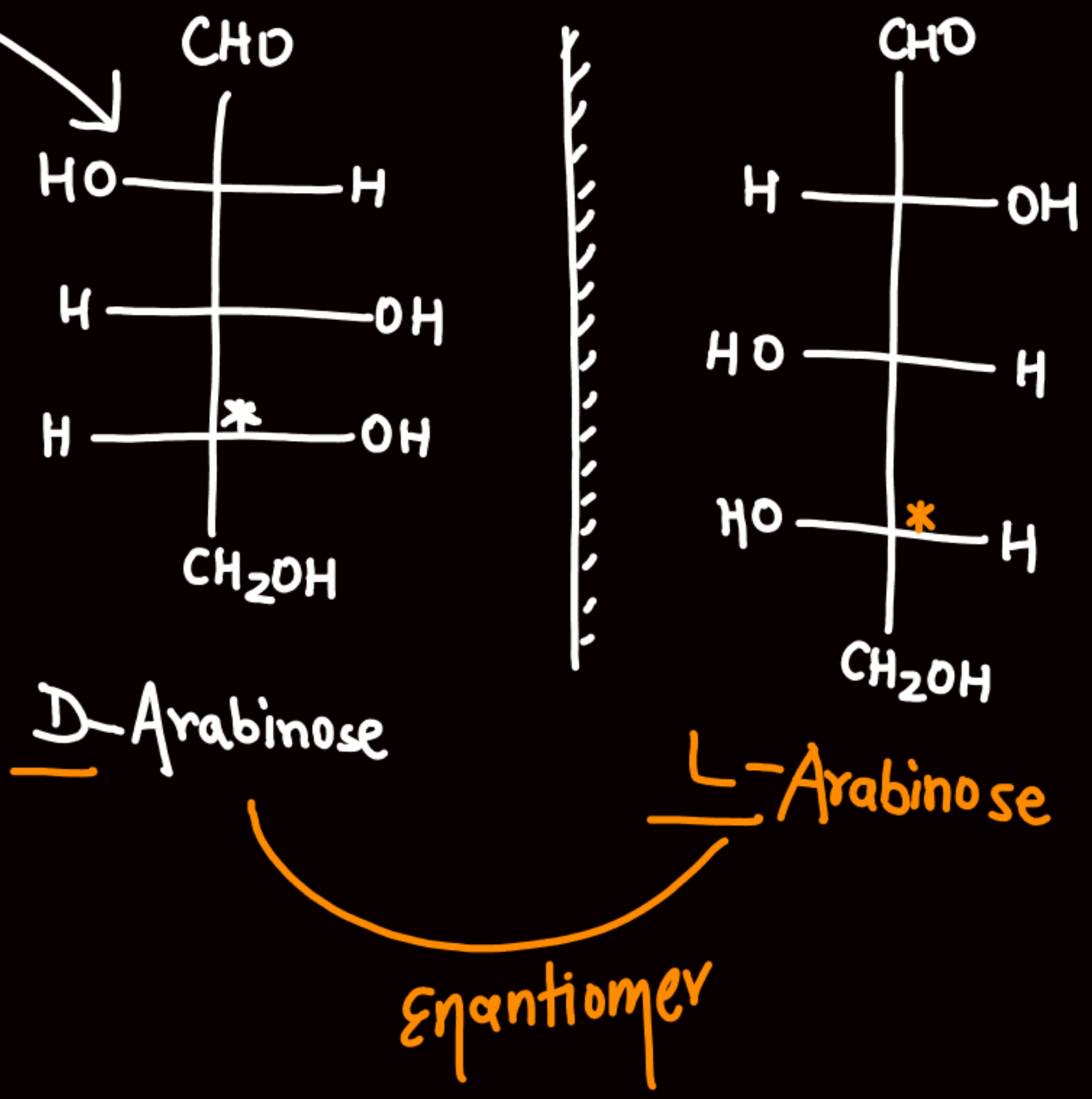
L Threose   D Threose

Enantiomers

③ Aldopentose

opp configuration at 1st chiral center.



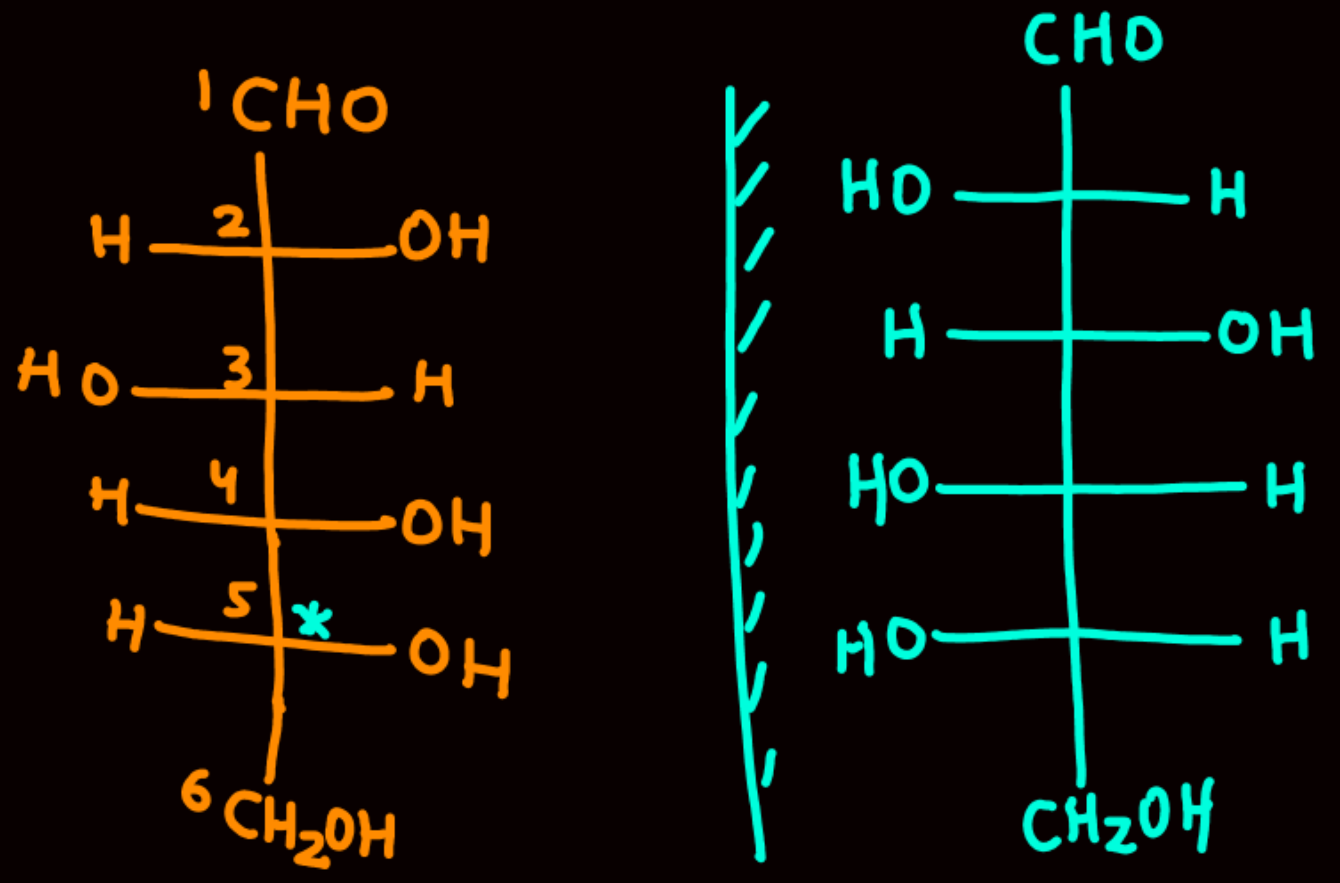


④ Aldohexose → opp configuration at 3rd carbon (2nd chiral carbon)

- Aldo → aldehyde
- hex → 6 carbon
- ose → carbohydrate

↳ Glucose is always dextrorotatory (d/+)

↳ also k/a Dextrose.



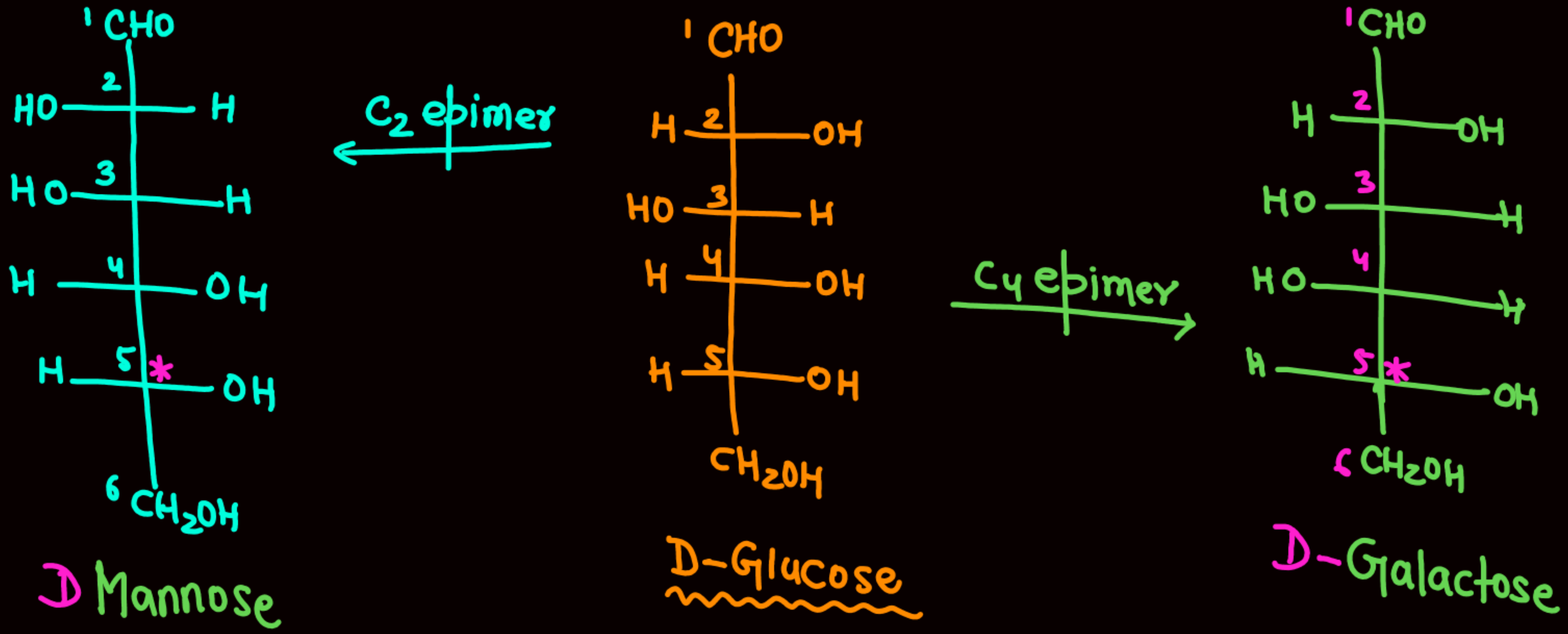
D Glucose L Glucose

Enantiomer

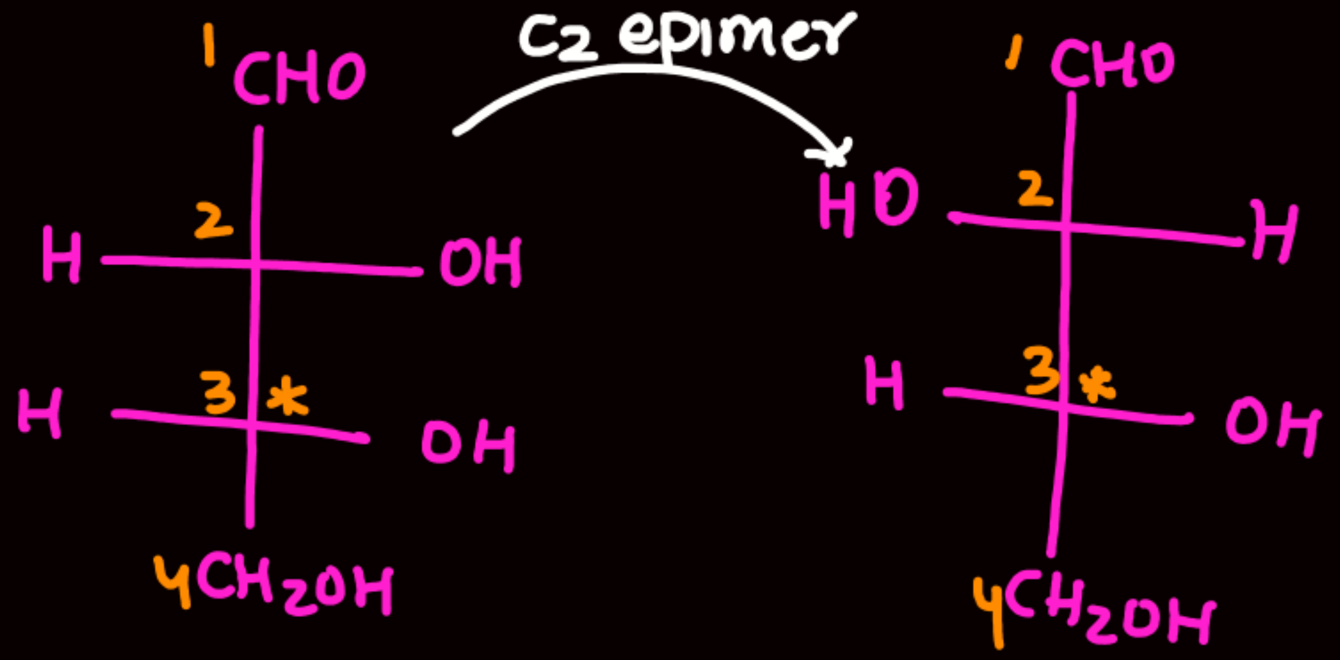
L Glucose → Hazardous to Health.

EPIMER

→ If there is a change in configuration at any one chiral center, then it is called epimer.



Que

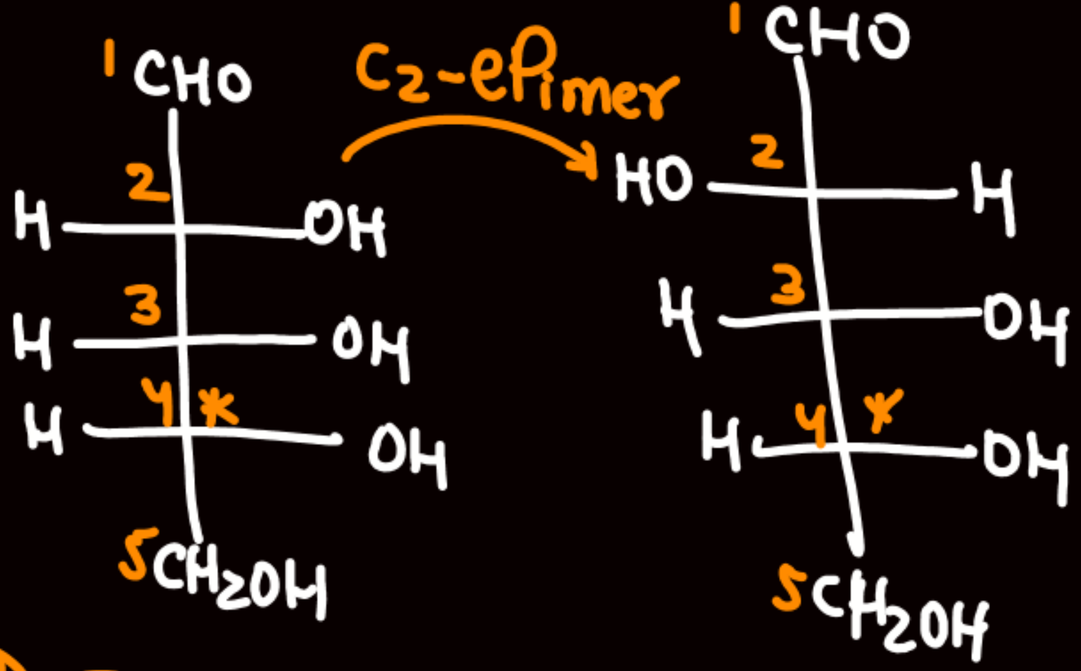


D-Erythrose D-Threose

What is the Relation b/w the Compound -

C_2 epimer

Que



D-Ribose D-Arabinose

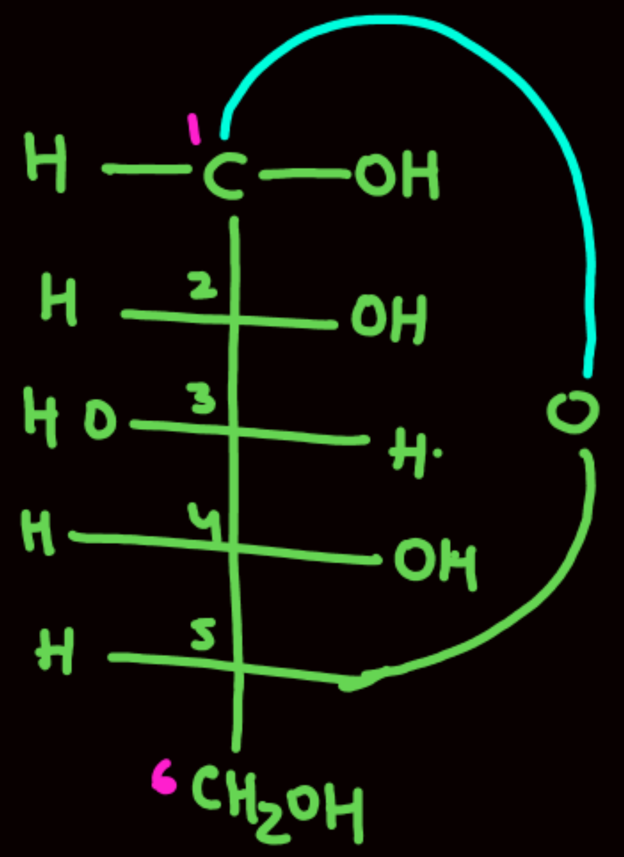
ANOMER

$R-\overset{O}{\overset{\|}{C}}-H + R'OH \rightarrow R-\overset{OH}{\underset{OR'}{C}}-H$ Hemi acetal

aldehyde alcohol

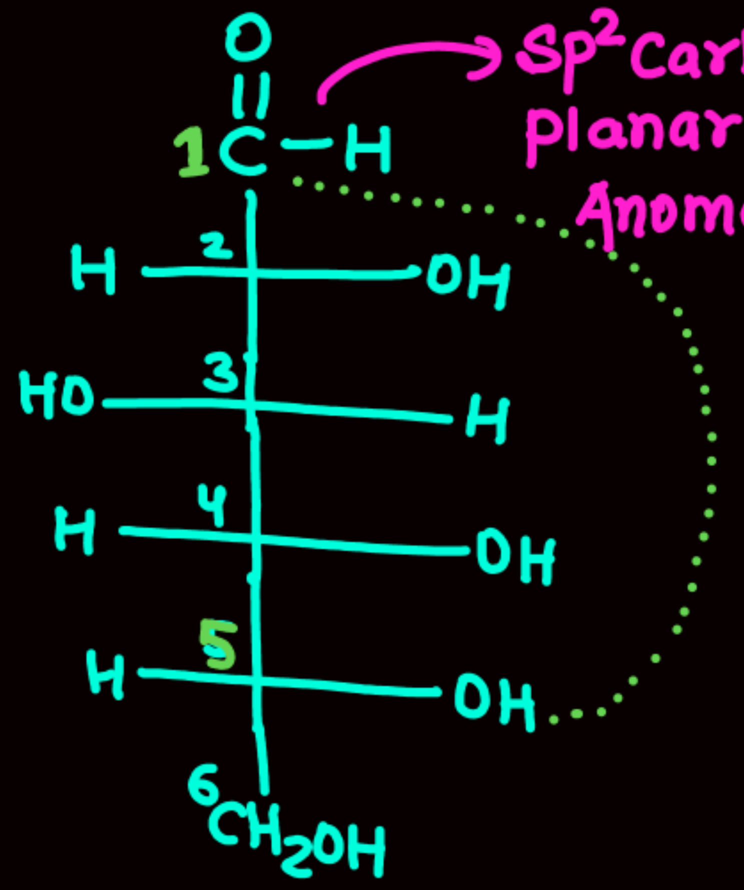
$R-\overset{O}{\overset{\|}{C}}-R + R'-OH \rightarrow R-\overset{OH}{\underset{OR'}{C}}-R$ Hemi ketal

Ketone alcohol



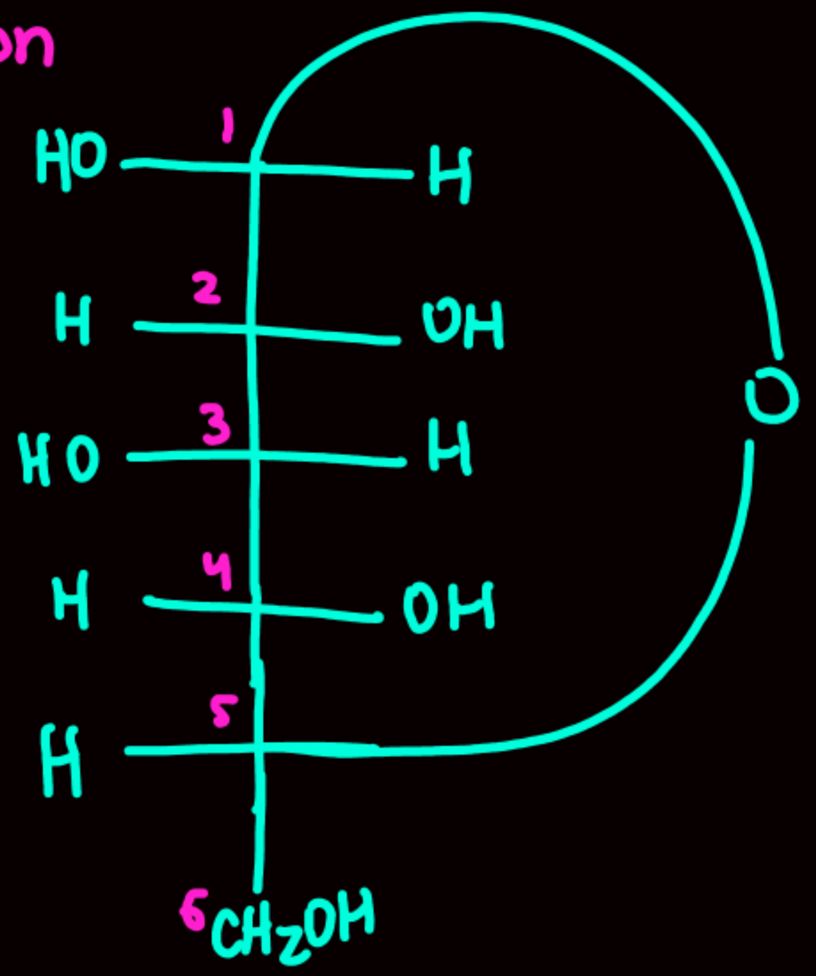
anomer (Hemiacetal)

α-D Glucose (MP → 419 K) (36%)



D-Glucose

(0.02%)



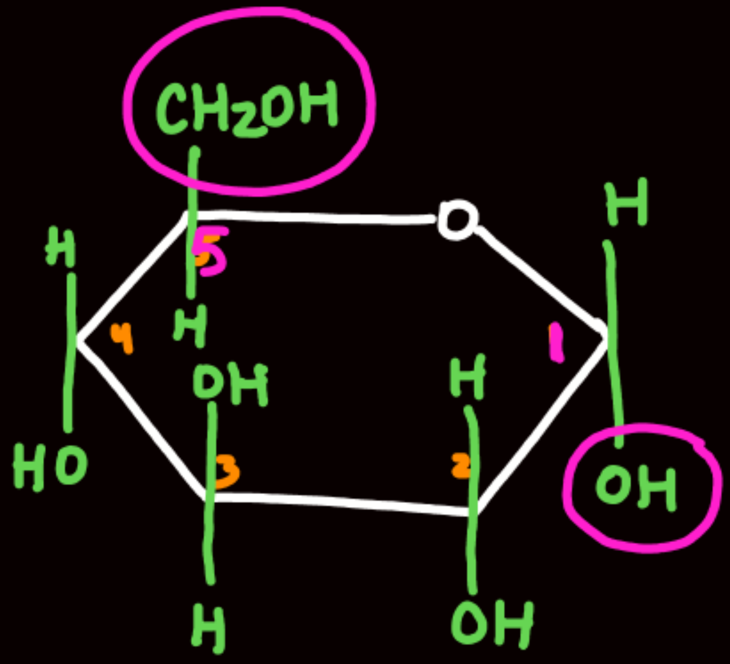
β-D-Glucose

(MP 423 K)

(64%)

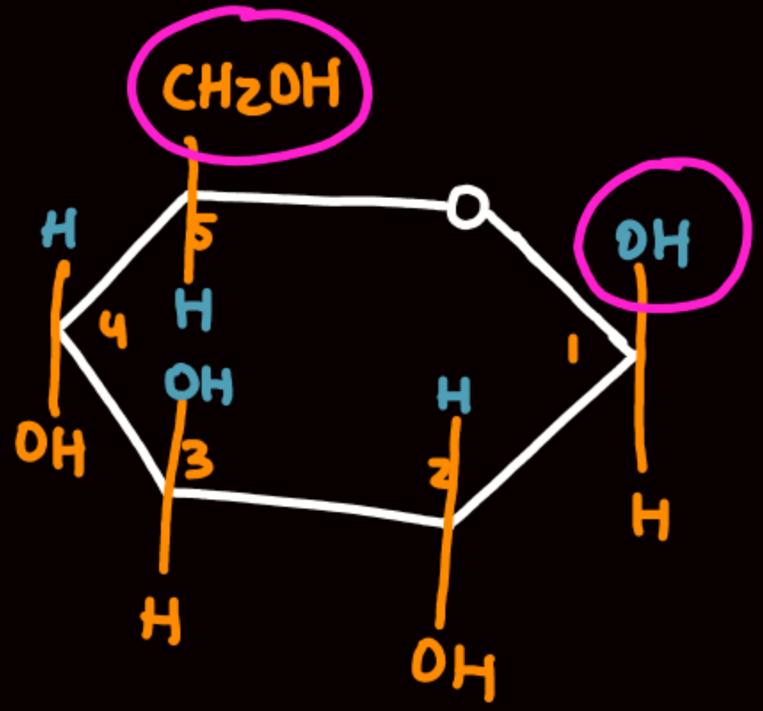
<u>note</u> → all anomers are epimers at 1st Carbon.

Cyclic Str of anomer of Glucose



α – D-Glucose

1^{st} Carbon – OH }
Last Carbon – OH } Trans → (α)



β – D - Glucose

1^{st} Carbon – OH }
Last Carbon – OH } Cis → (β)

} Pyranose Ring Structure

⇓

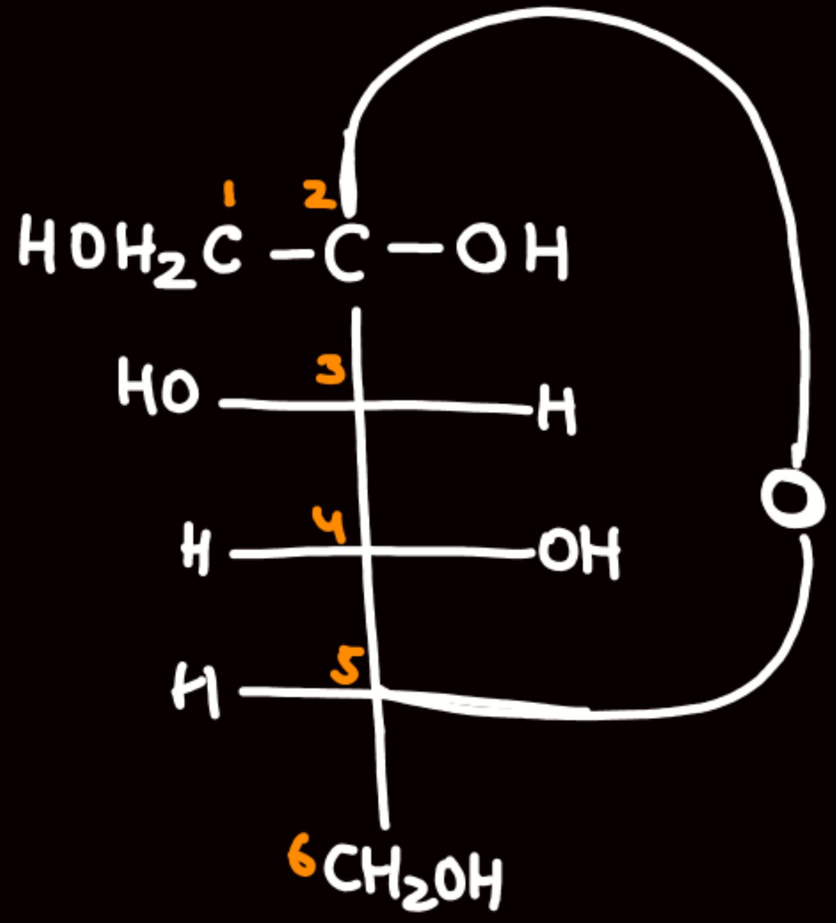
Haworth Str



Pyran

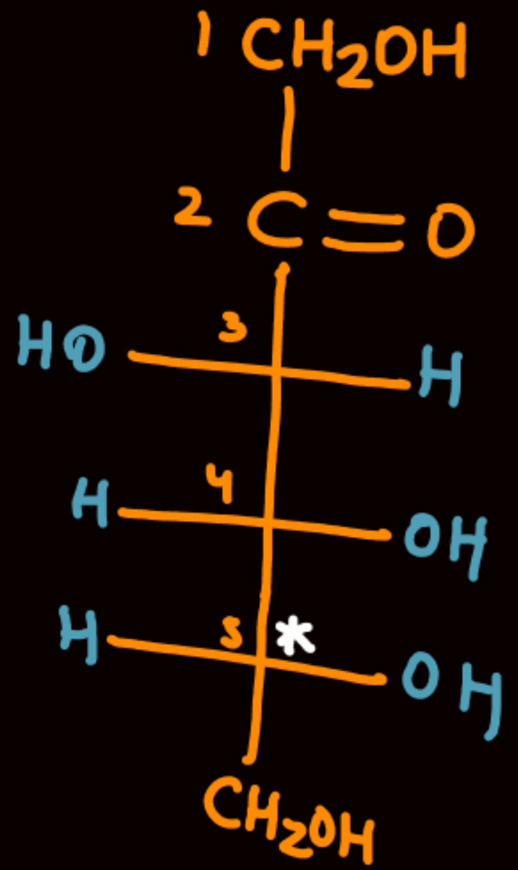
FRUCTOSE

(Ketohexose)

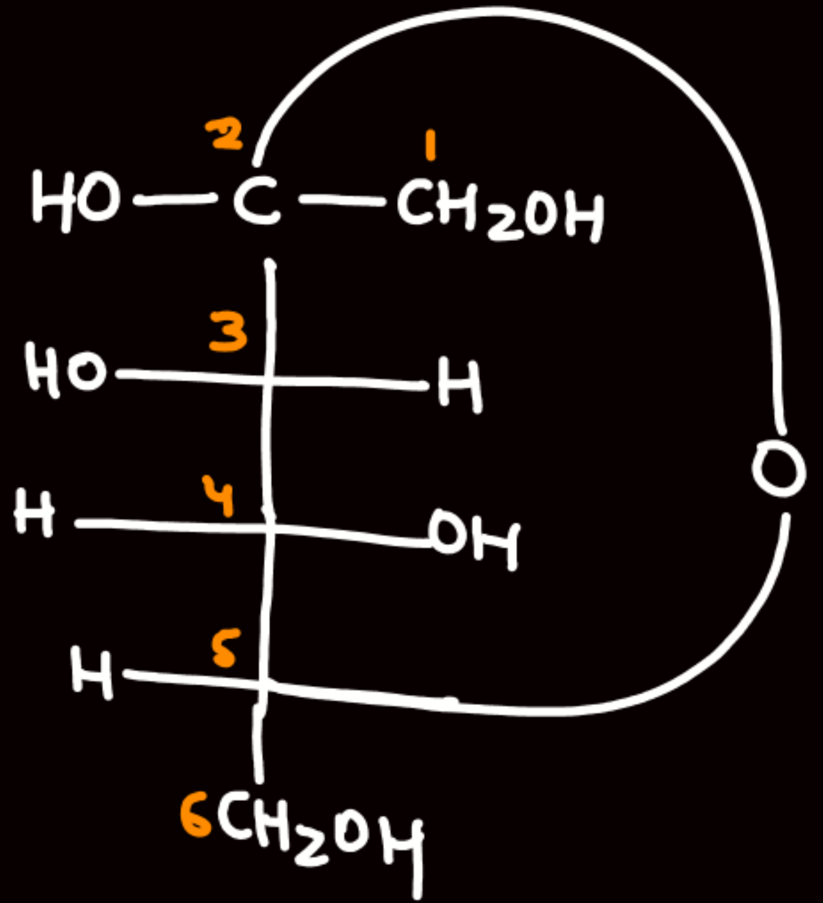


$C_2 - C_5$ Hemiketal

α-D Fructose



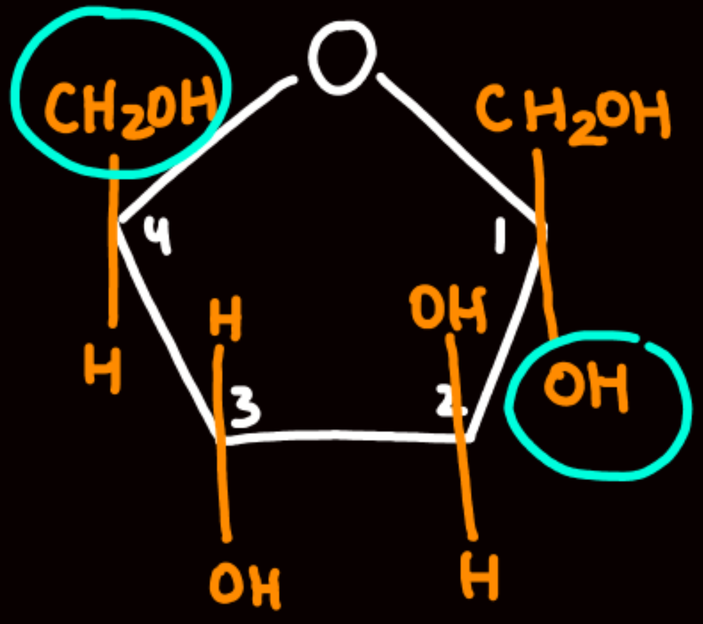
D-Fructose



$C_2 - C_5$ Hemiketal

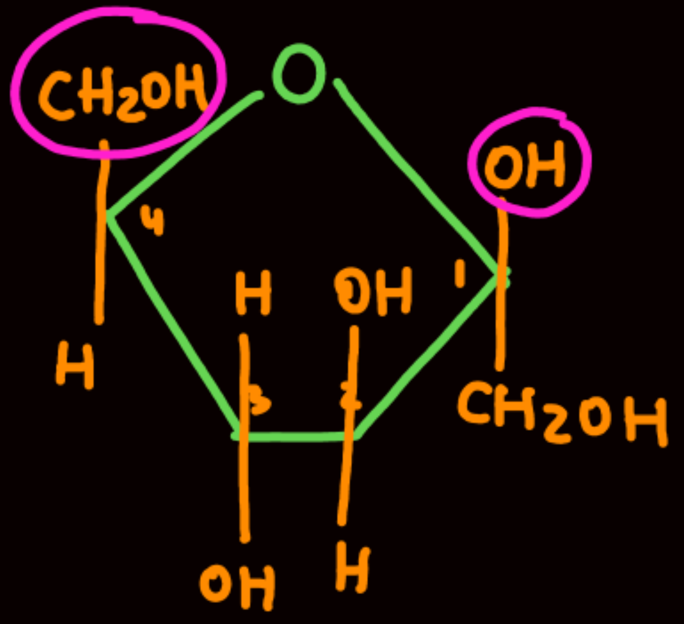
β-D-Fructose

Cyclic str of anomer of Fructose



1st Carbon —OH
Last Carbon—OH } Trans

α-D-Fructose



1st Carbon —OH
Last Carbon—OH } Cys

β-D-Fructose



Furan

BIOMOLECULES

Carbohydrates

Biomolecule — 80% weightage Carbohydrate.

Old def: $C_x(H_2O)_y \rightarrow$ Carbohydrate

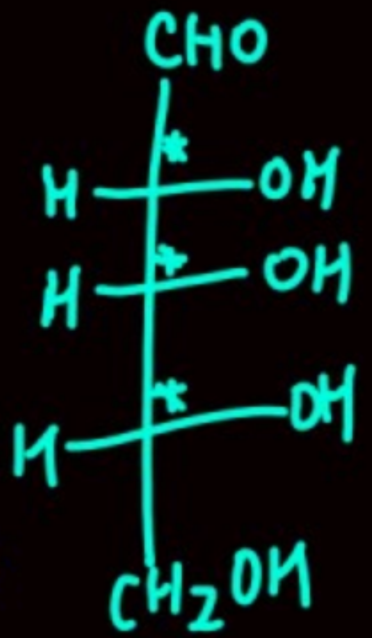
eg. $C_6H_{12}O_6 \rightarrow C_6(H_2O)_6$ ⎫
$C_{12}H_{22}O_{11} \rightarrow C_{12}(H_2O)_{11}$ ⎭ Carbohydrate

$CH_3COOH \rightarrow C_2(H_2O)_2$ } not Carbohydrate
Acetic acid

$C_6H_{12}O_5 \longrightarrow$ ✕ } Carbohydrate
Rhamnose

New def:

* optically active compound, which contains polyhydroxy aldehyde or poly hydroxy ketone are called Carbohydrates.
* comp which produces poly Hydroxy aldehyde/ketone on Hydrolysis are called Carbohydrate.





✓⟶ Carbohydrates are also k/a Saccharides.

✓⟶ Carbohydrates which are sweet in taste are called Sugar.

(Classification) **Types of Carbohydrates.**

① polysaccharides

↓ H_3O^+

produces Hundreds molecules of Saccharides.

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↓ H_3O^+

produces 2-10 molecule of Saccharides

③ MonoSaccharides.

↓ H_3O^+

✗

(Basic unit of Carbohydrate)

* Saccharides Containing aldehyde group ⟶ Aldose

" " ketone " ⟶ ketose

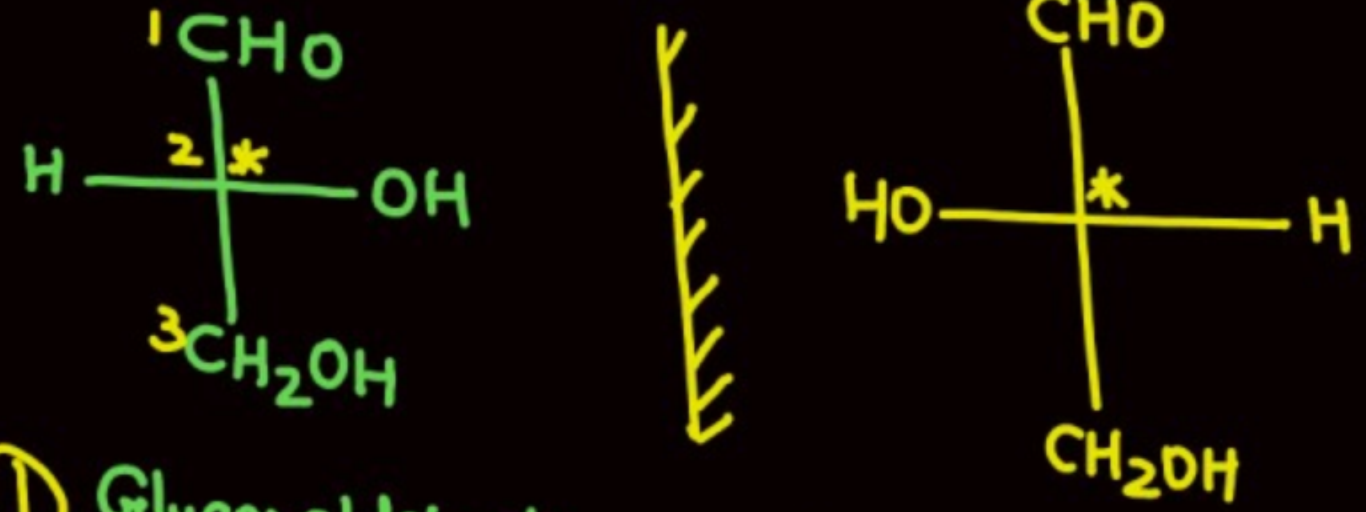
(ose)

OTSE

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- tri → 3 carbon
- ose → saccharides (carbohydrates)

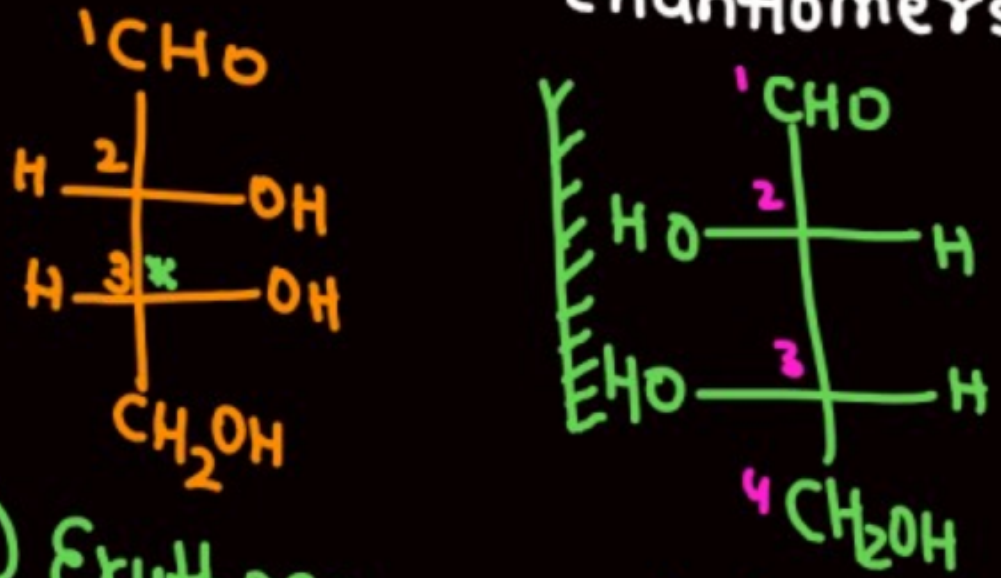


D Glyceraldehyde — L Glyceraldehyde

Enantiomers

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D Erythose — L Erythrose

Enantiomer.

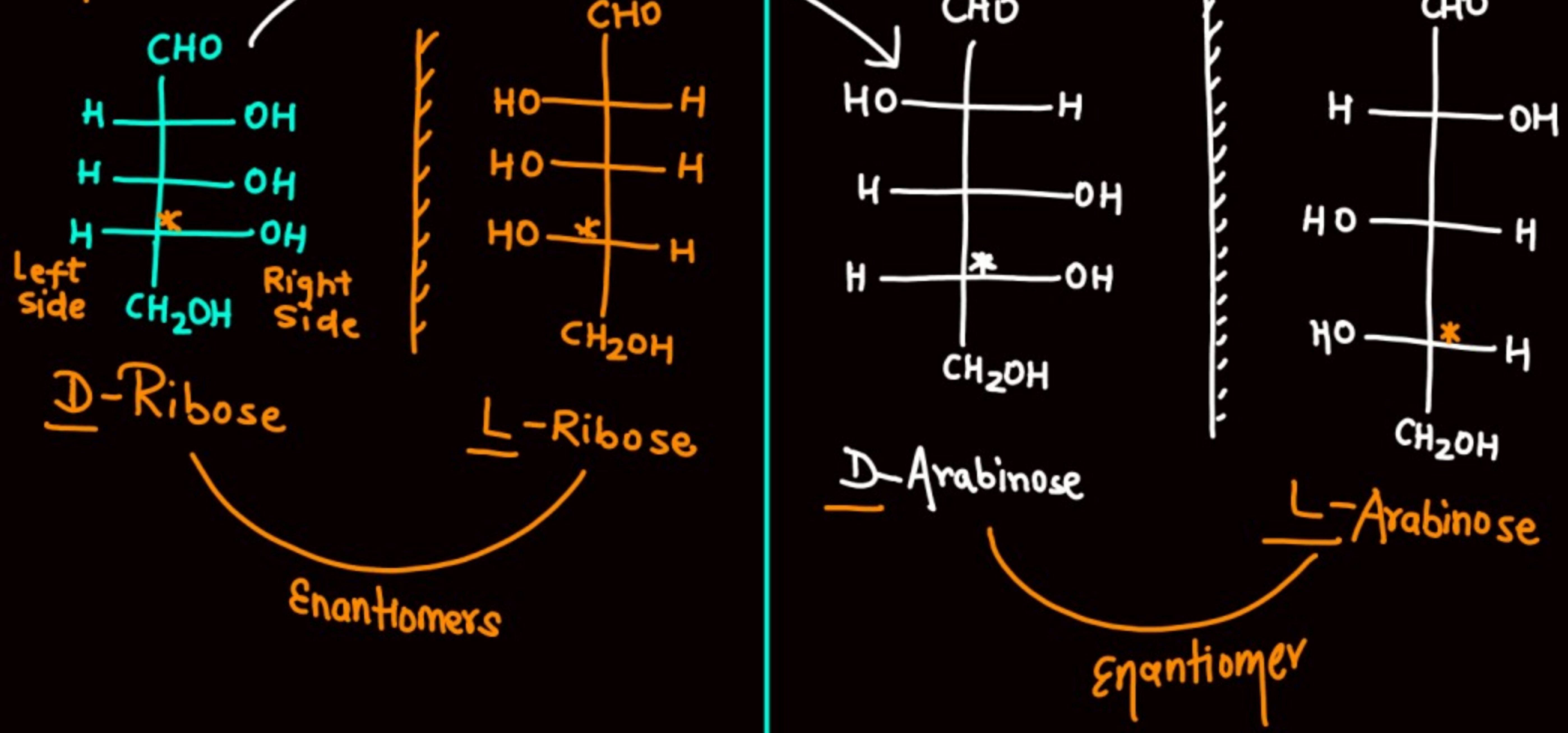


L Threose — D Threose

Enantiomers

(3) Aldopentose

opp configuration at 1st chiral center.



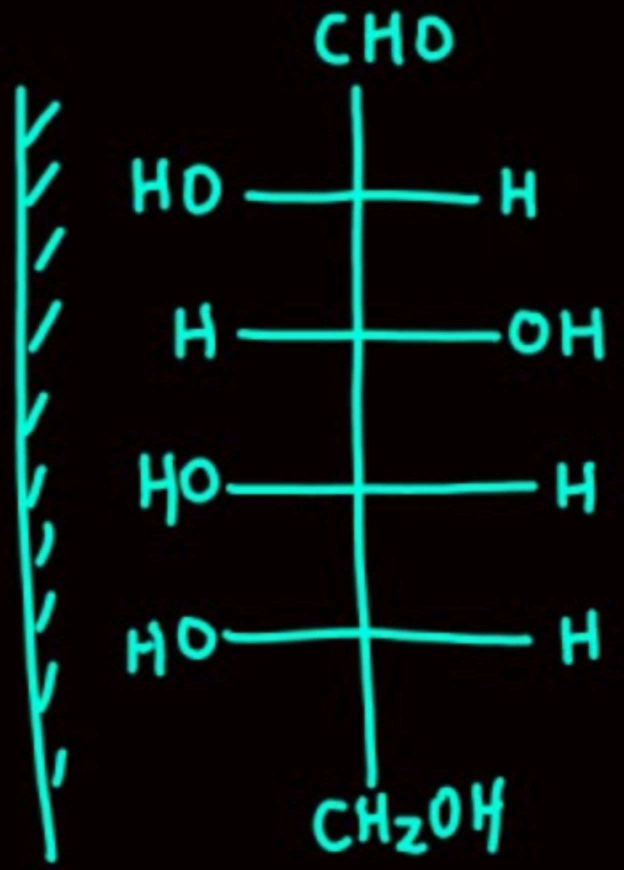
④ Aldohexose → opp configuration at 3rd carbon (2nd chiral carbon)

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↳ Glucose is always dextrorotatory (d/+)

↳ also k/a Dextrose.





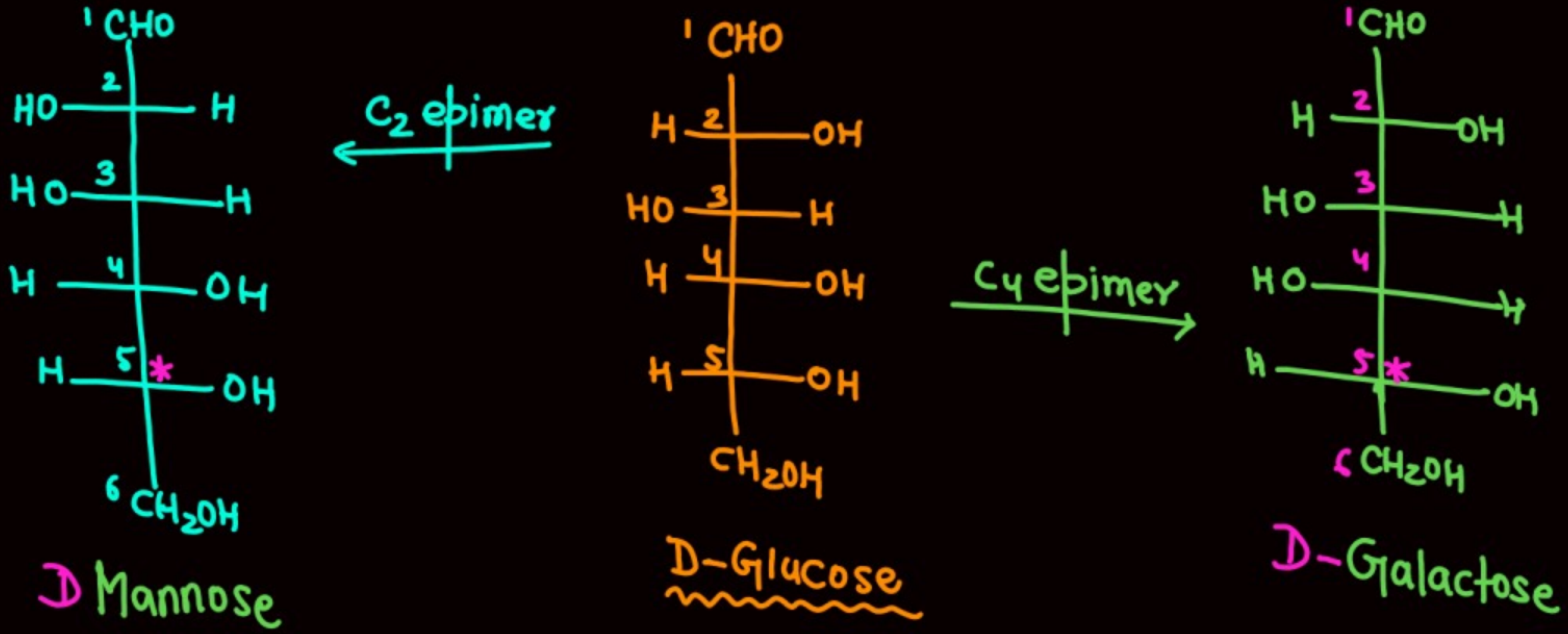
D Glucose — L Glucose

Enantiomer

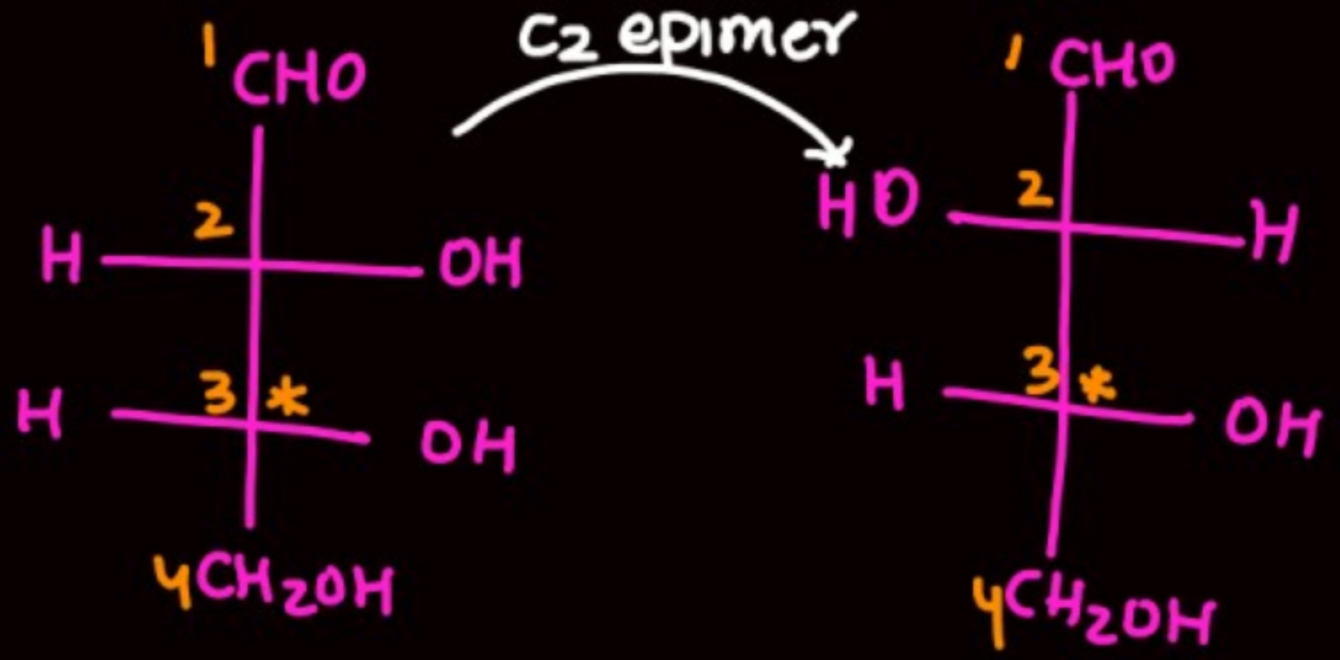
L Glucose → Hazardous to Health.

EPIMER

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Que

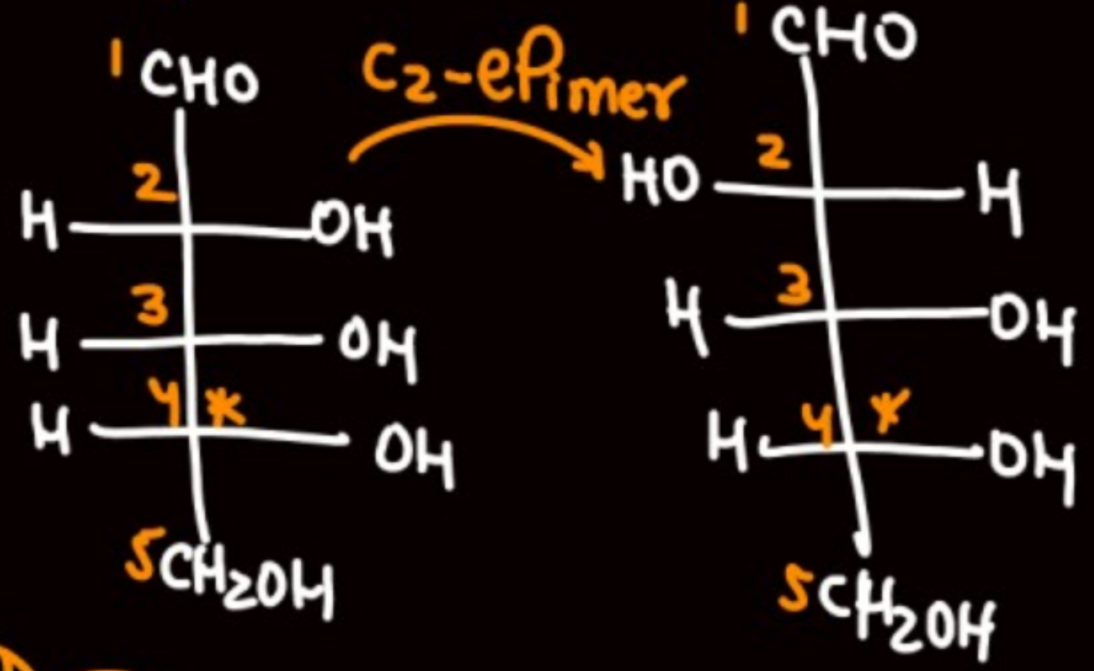


D-Erythrose　　D-Threose

What is the Relation b/w the Compound -

C_2 epimer

Que



D-Ribose　　D-Arabinose

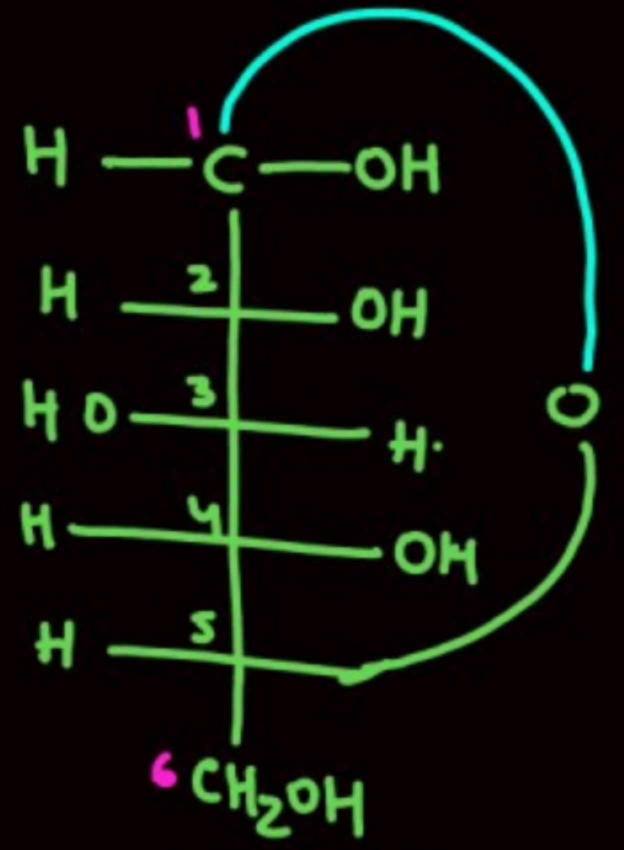
ANOMER

$$R-\overset{O}{\overset{\|}{C}}-H + R'OH \rightarrow R-\underset{OR'}{\overset{OH}{C}}-H$$

aldehyde alcohol → Hemi acetal

$$R-\overset{O}{\overset{\|}{C}}-R + R'-OH \rightarrow R-\underset{OR'}{\overset{OH}{C}}-R$$

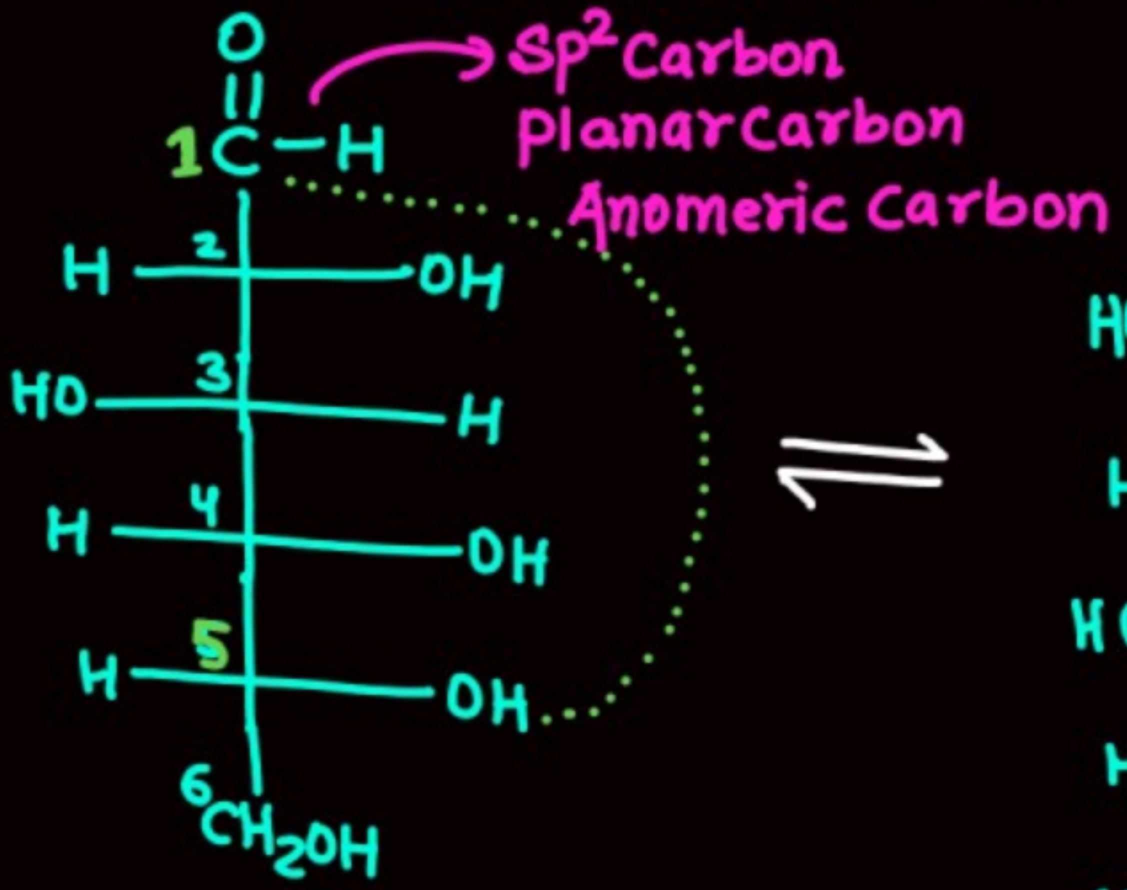
Ketone alcohol → Hemi ketal



anomer (Hemiacetal)

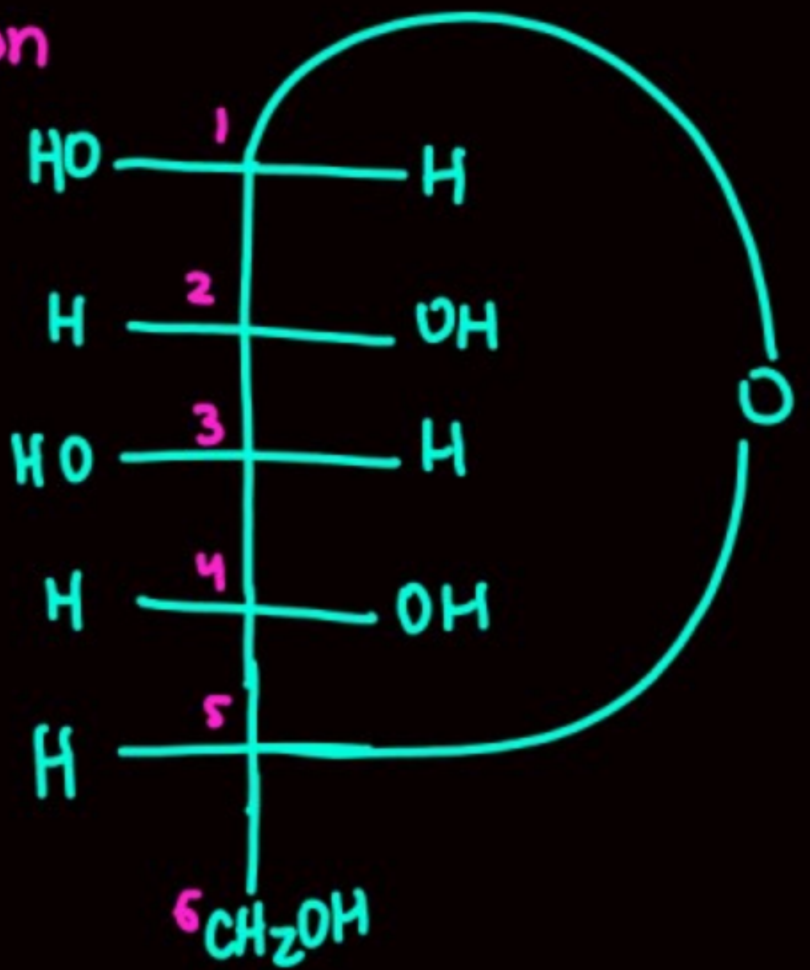
α-D Glucose (MP→419k) (36%)

⇌



D-Glucose (0.02%)

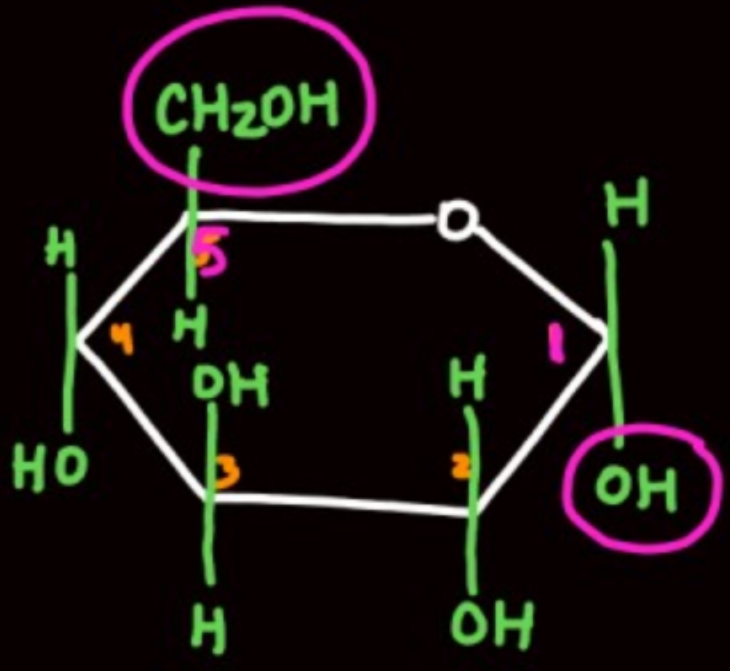
⇌



β-D-Glucose (MP 423k) (64%)

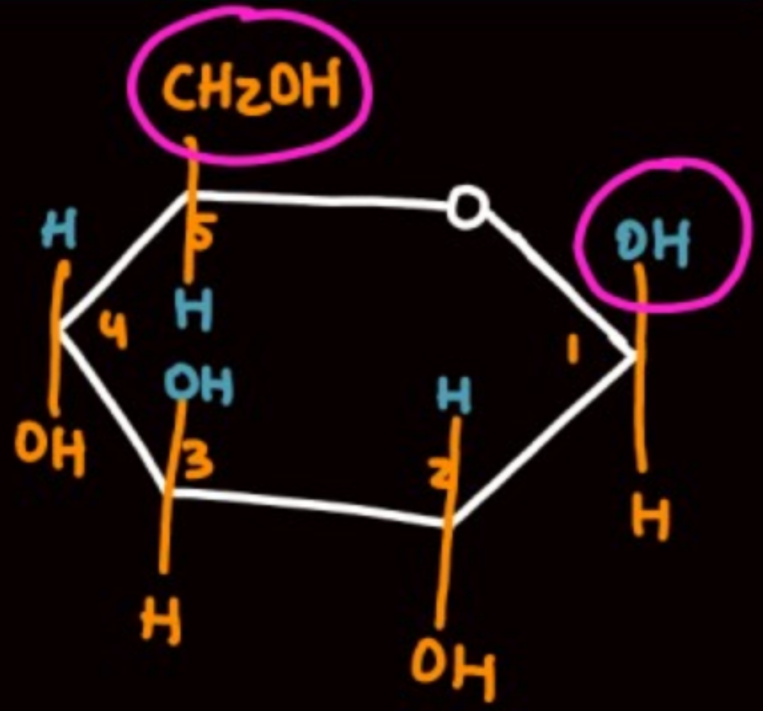
<u>note</u> → all anomers are epimers at 1st Carbon.

Cyclic Str of anomer of Glucose



α – D-Glucose

1st Carbon–OH
Last Carbon–OH } Trans
↓
(α)



β – D – Glucose

1st Carbon–OH
Last Carbon–OH } Cys
↓
(β)

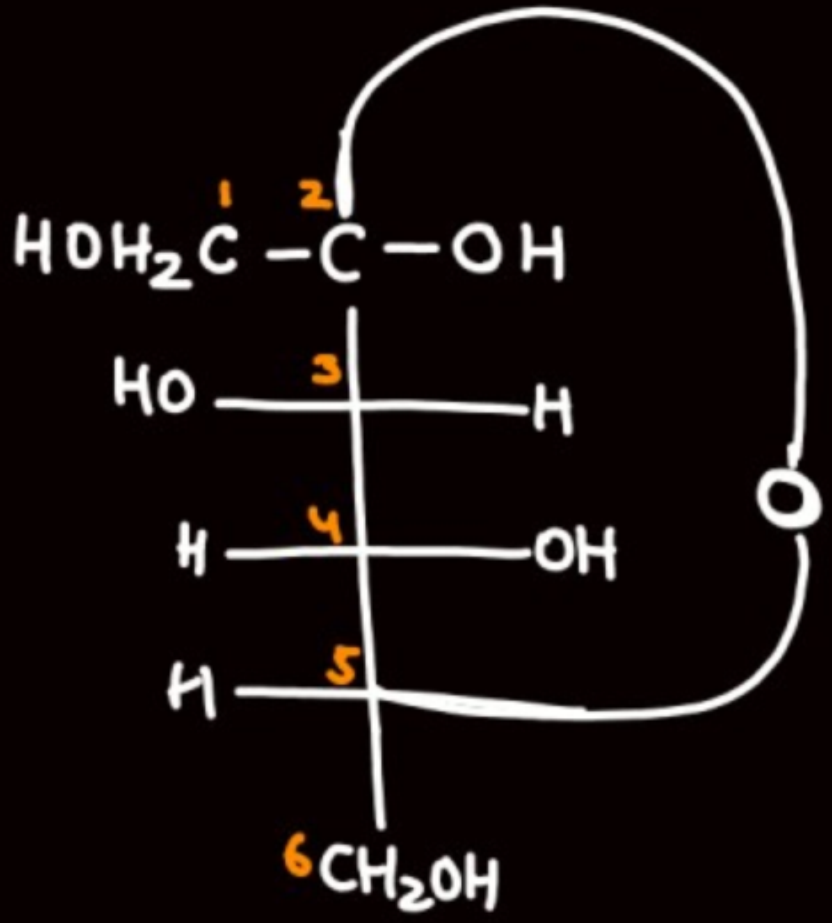
} Pyranose Ring Structure
⇓
Haworth Str



Pyran

FRUCTOSE

(Ketohexose)

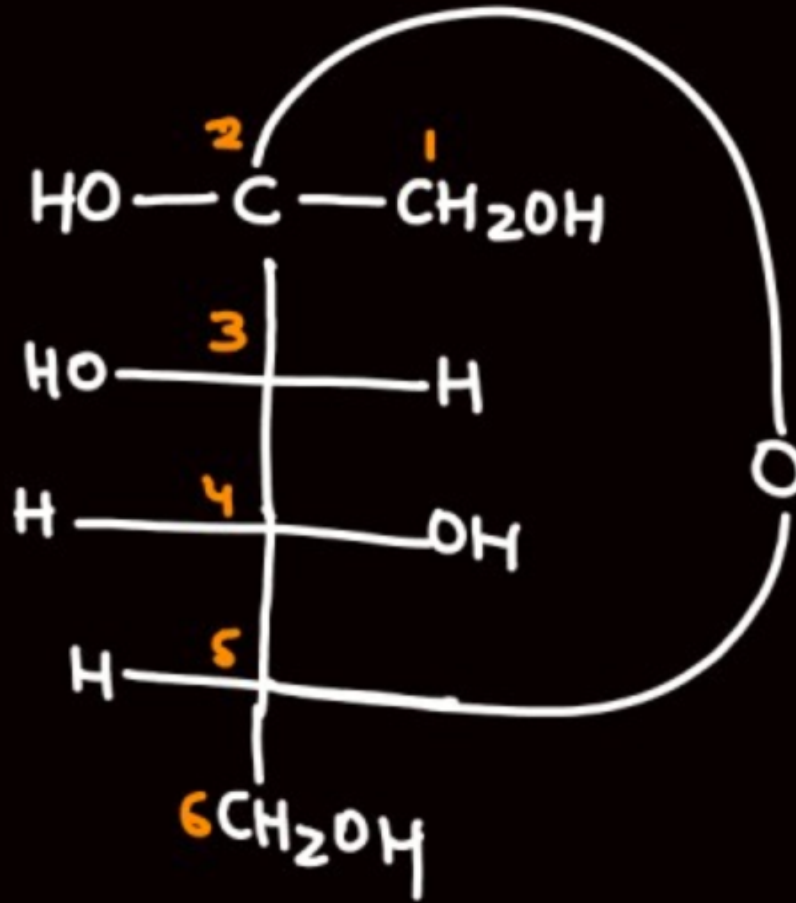


$C_2 - C_5$ Hemiketal

α-D Fructose



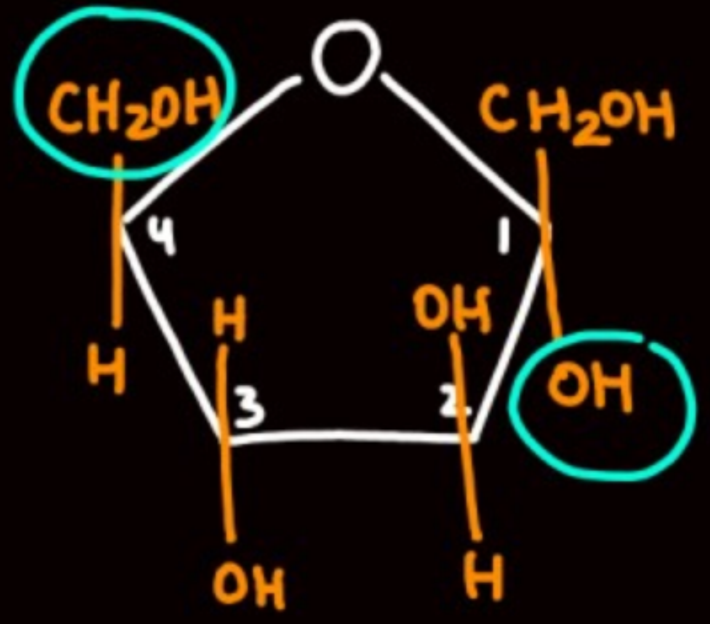
D-Fructose



$C_2 - C_5$ Hemiketal

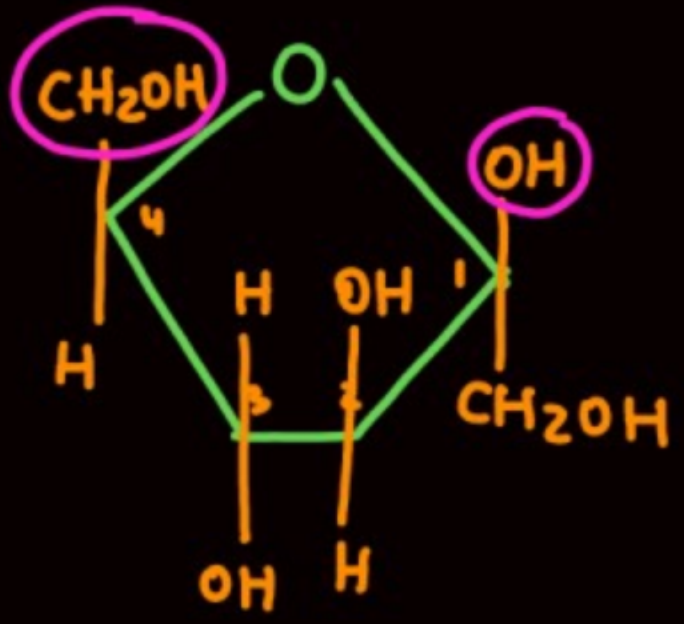
β-D-Fructose

Cyclic str of anomer of Fructose



1st Carbon —OH
Last Carbon—OH } Trans

α-D-Fructose



1st Carbon —OH
Last Carbon—OH } cys

β-D-Fructose

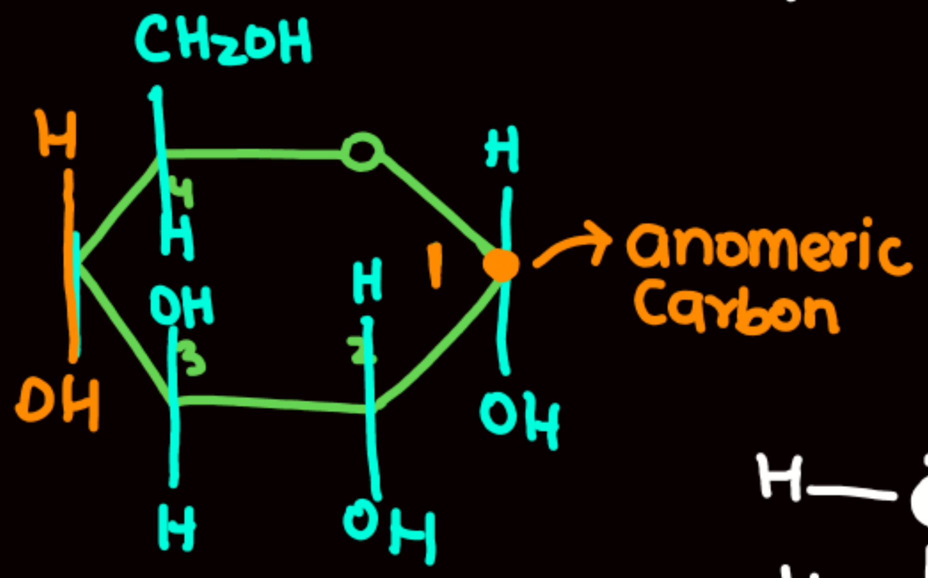


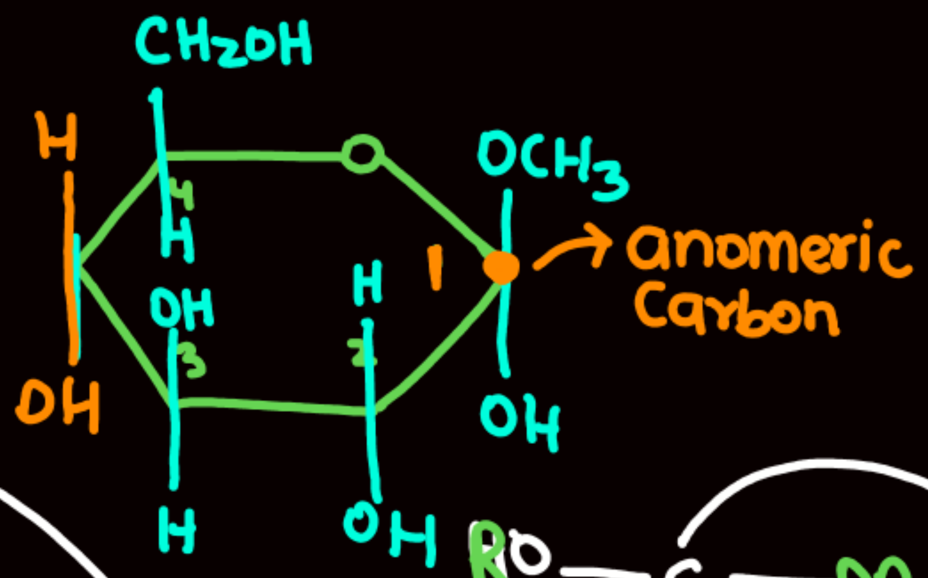
Furan

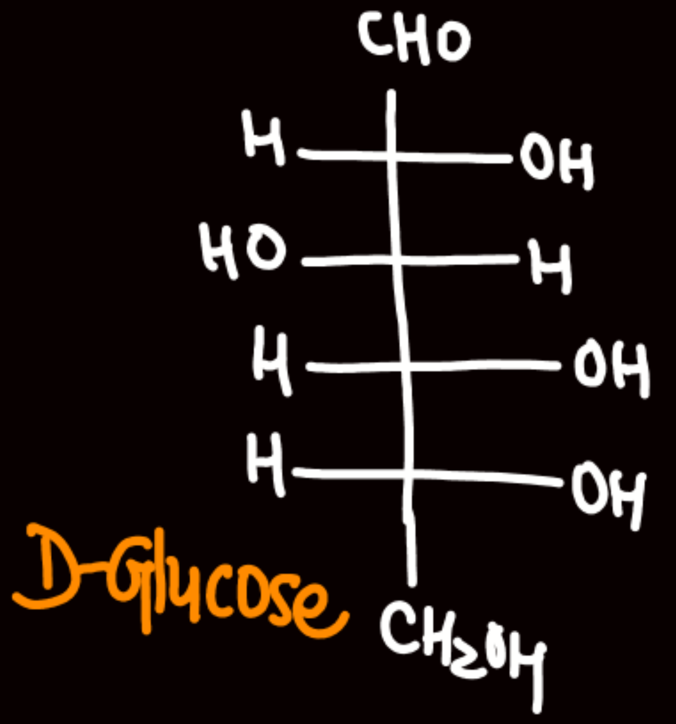
Reducing & NON Reducing Sugar

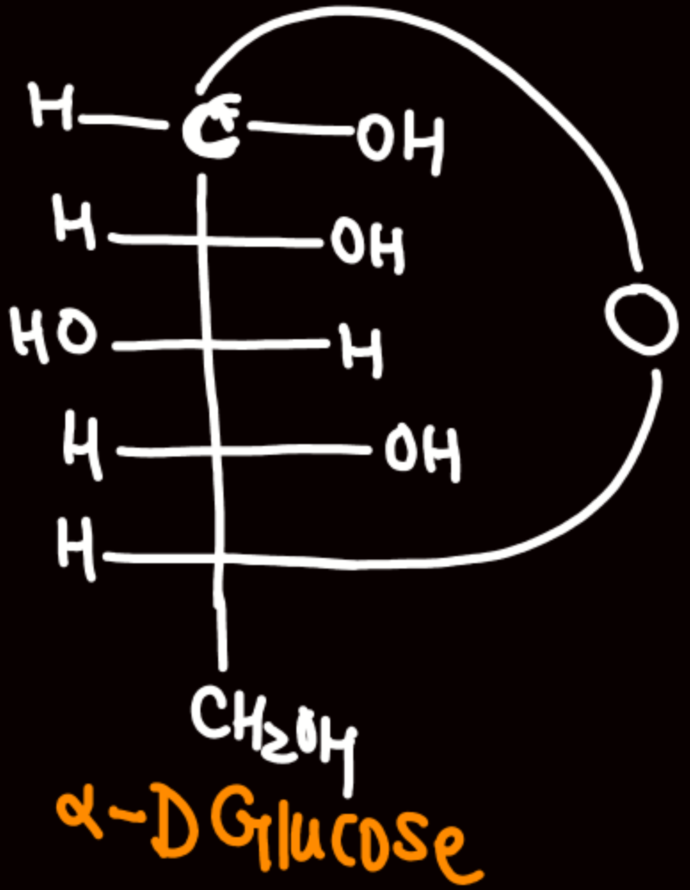
Reducing Sugar: Carbohydrate which Contains H & OH on anomeric Carbon.

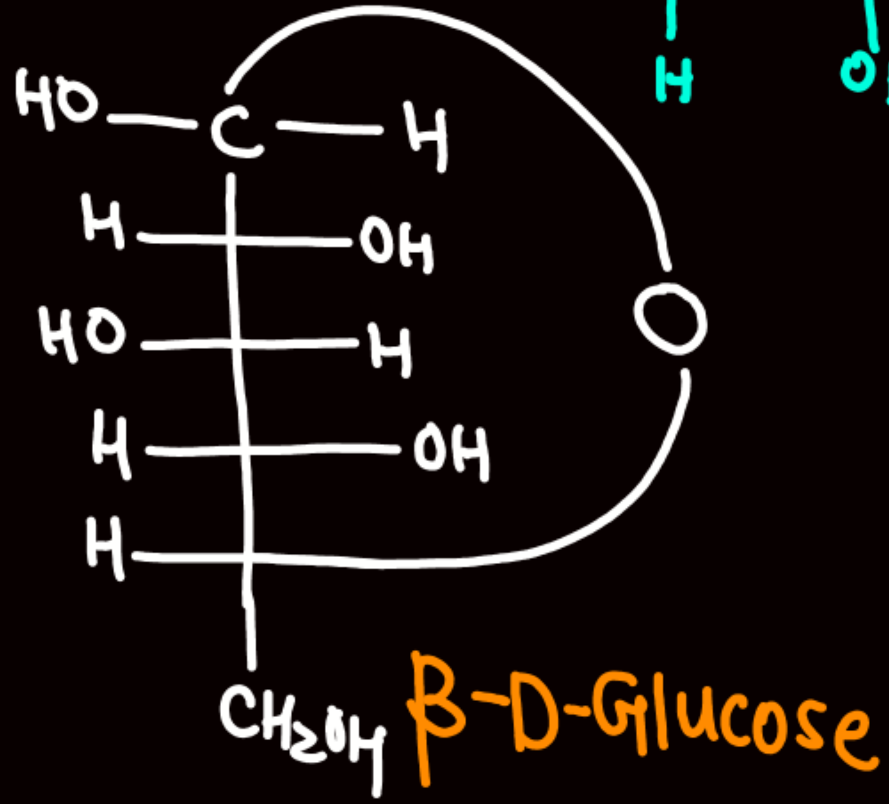
Non Reducing Sugar: Carbohydrate which do not contain H & OH at anomeric carbon.

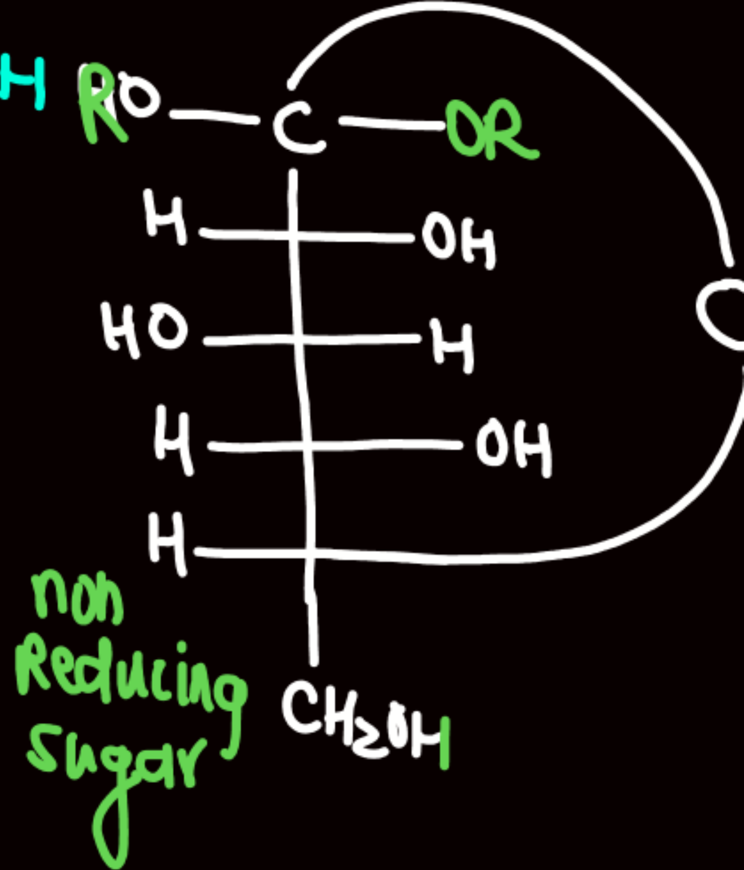






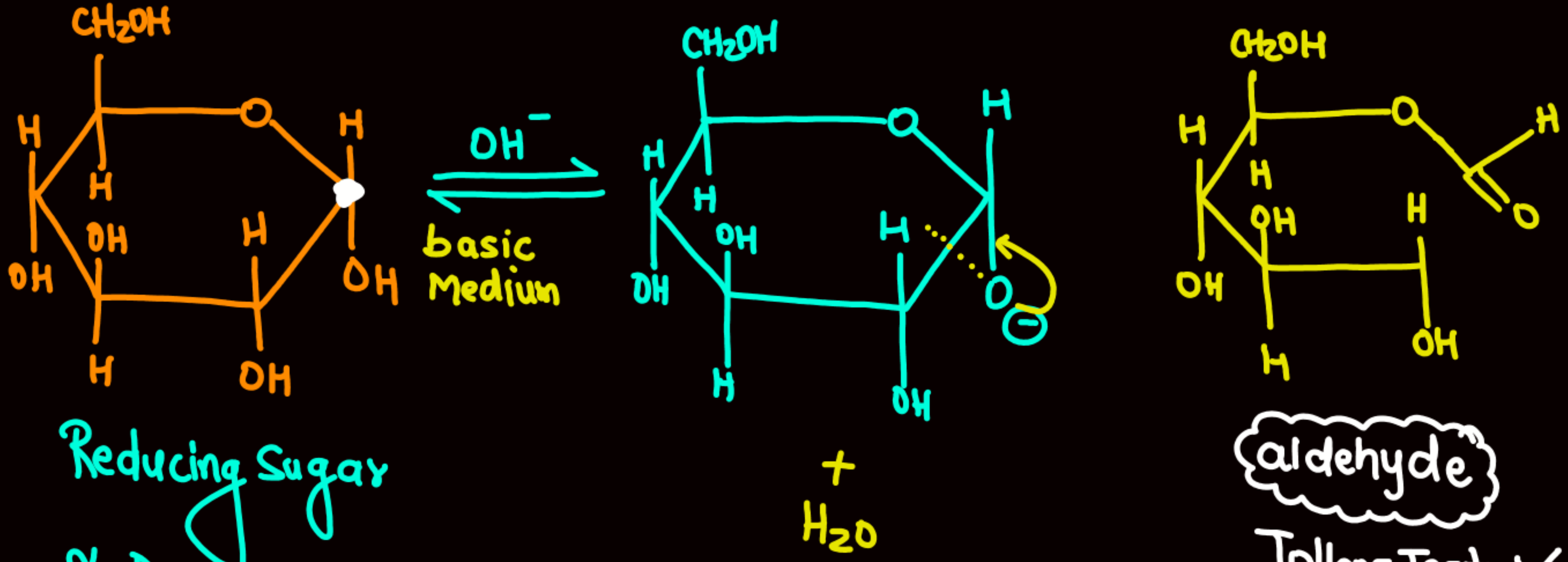






note : Reducing Sugar gives Tollen's Test, Fehling Test, Benedict Test...

Non Reducing Sugar donot give any of the above Test.



α-D-Glucose

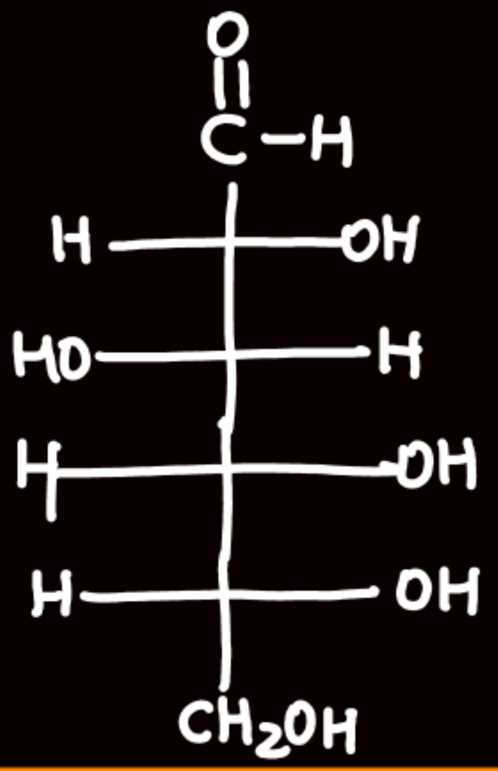
Tollens Test ✓

Fehling Test ✓

Benedict Test ✓

note Glucose & fructose both give Tollen's Test.

Fructose exists as Glucose & Mannose.

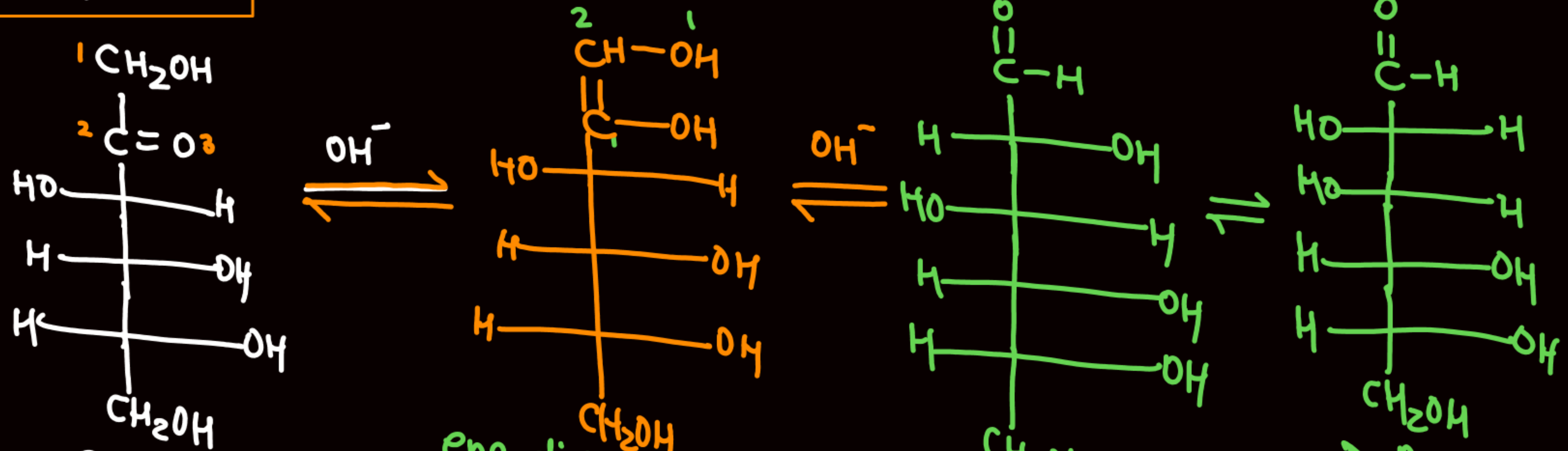


D Glucose

→ Tollen Test ✓

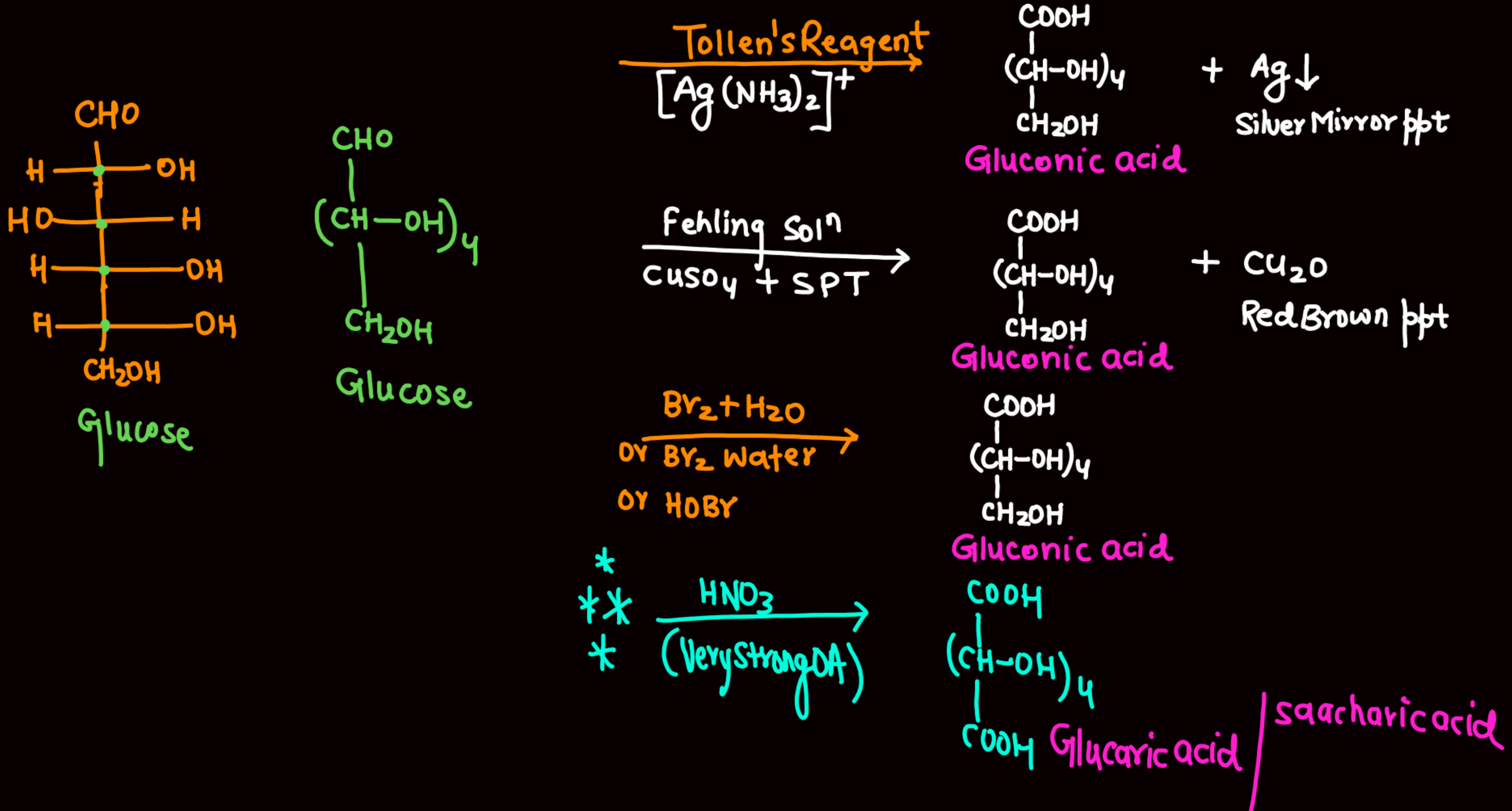
Fehling Test ✓ (bcoz aldehyde group is present)

Benedict Test ✓

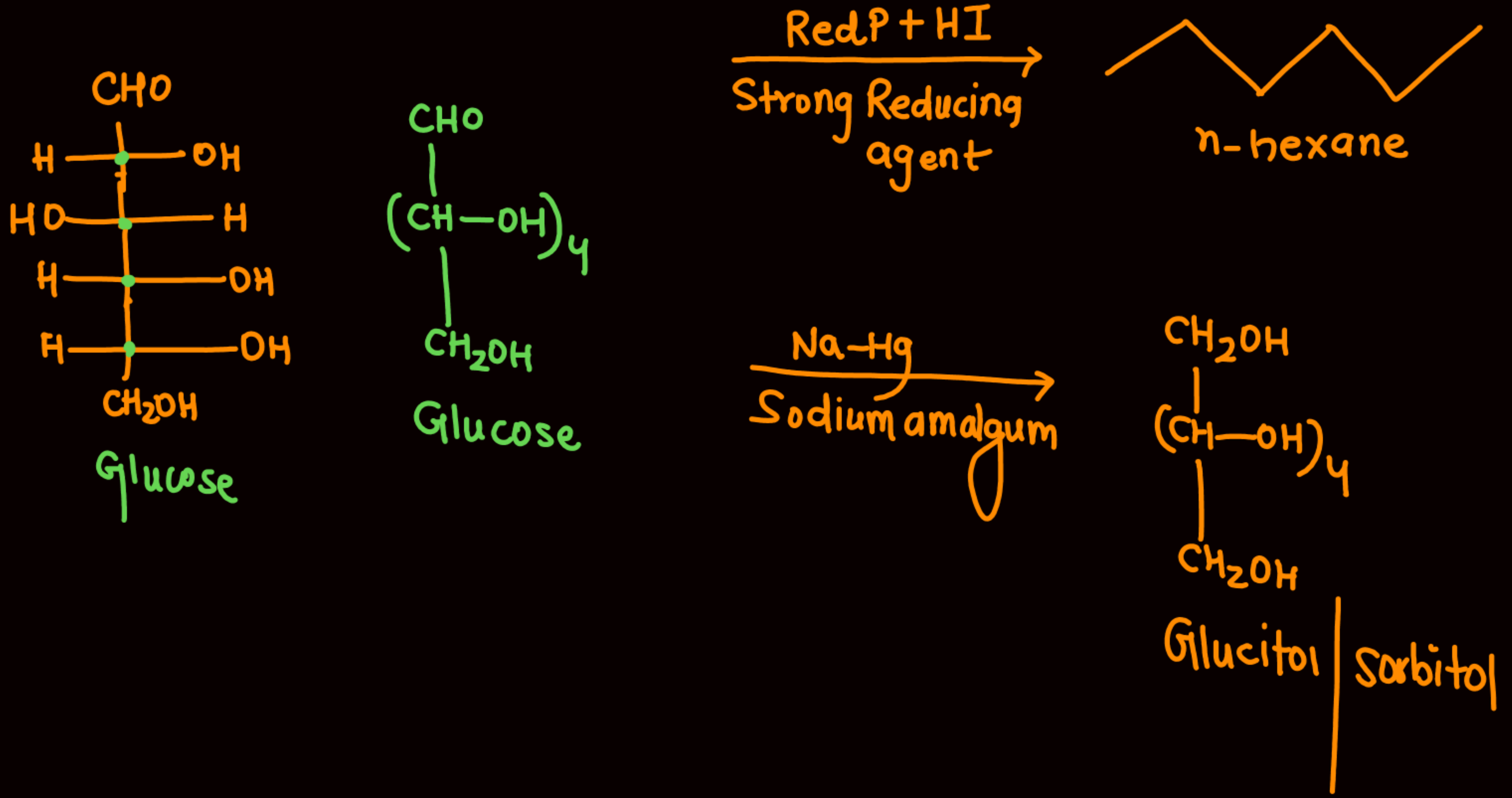


D-Fructose ⇌ ene-diol ⇌ D-Glucose ⇌ D-Mannose

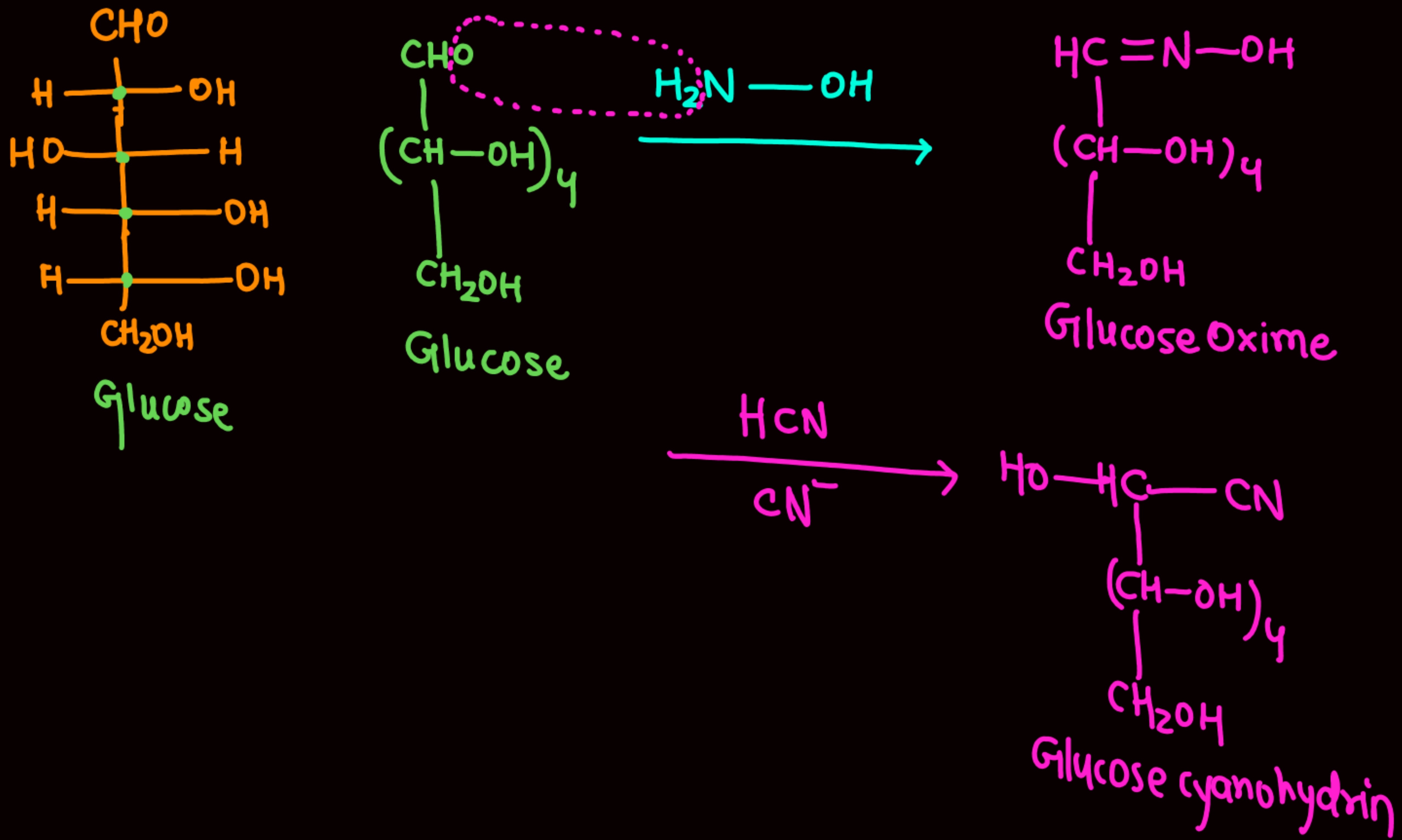
Test Of Glucose



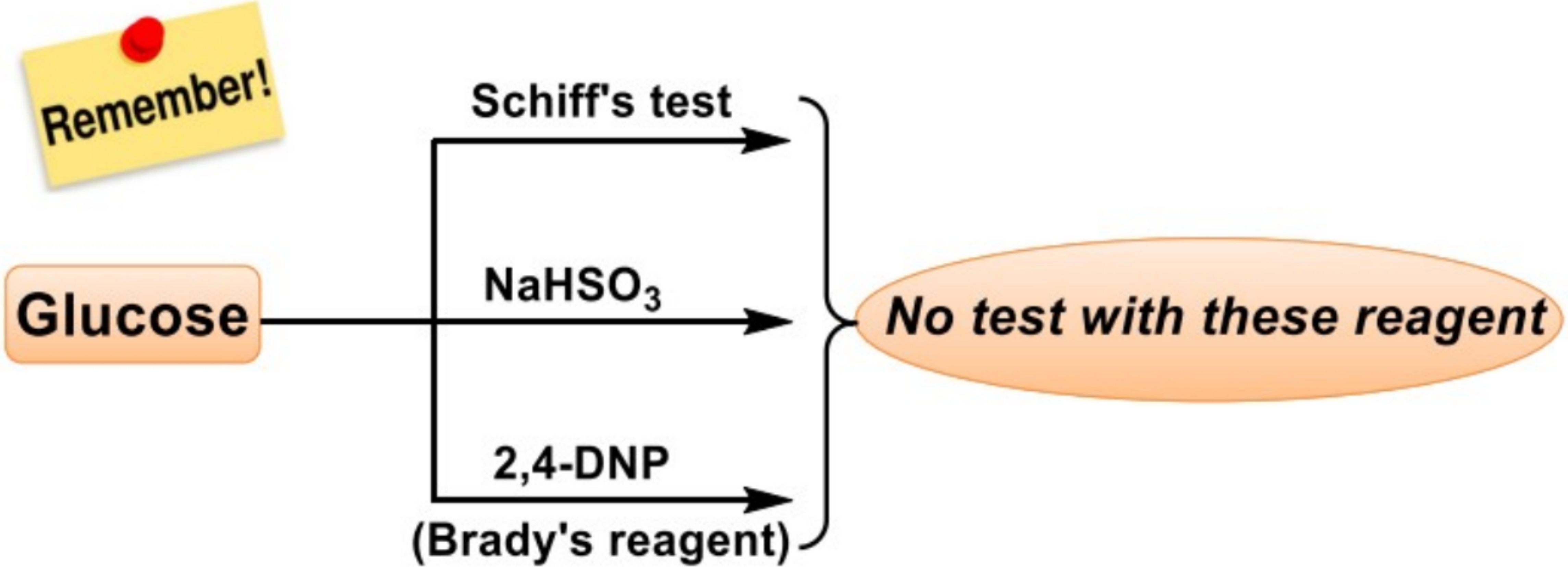
Reduction of Glucose



Reduction Of Glucose

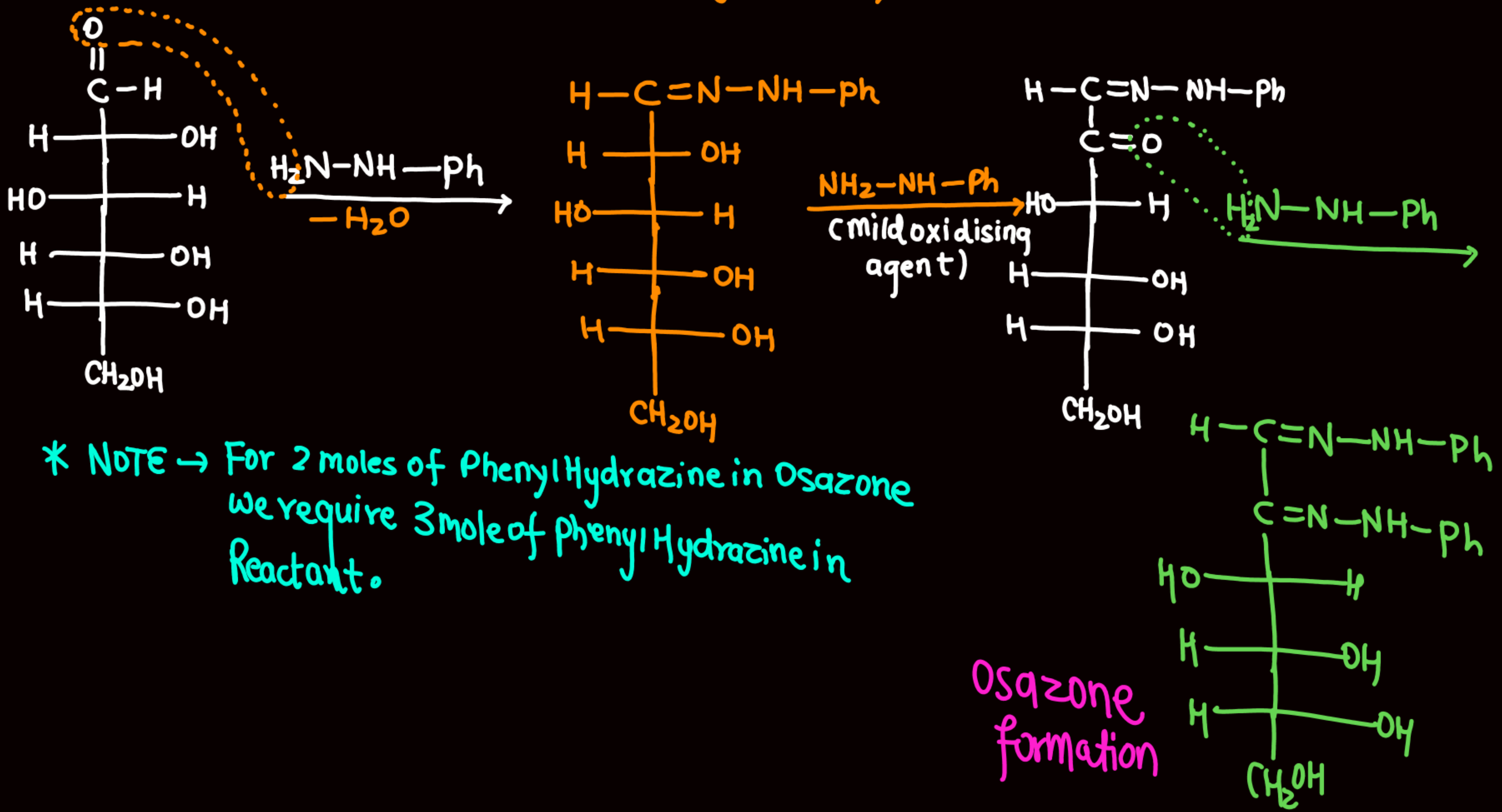


Important point about Glucose:



❖ **Pentaacetate of glucose does not react with hydroxylamine.**

Reaction with Phenyl Hydrazine / Osazone Formⁿ



* NOTE → For 2 moles of Phenyl Hydrazine in Osazone we require 3 mole of Phenyl Hydrazine in Reactant.

Di-saccharides

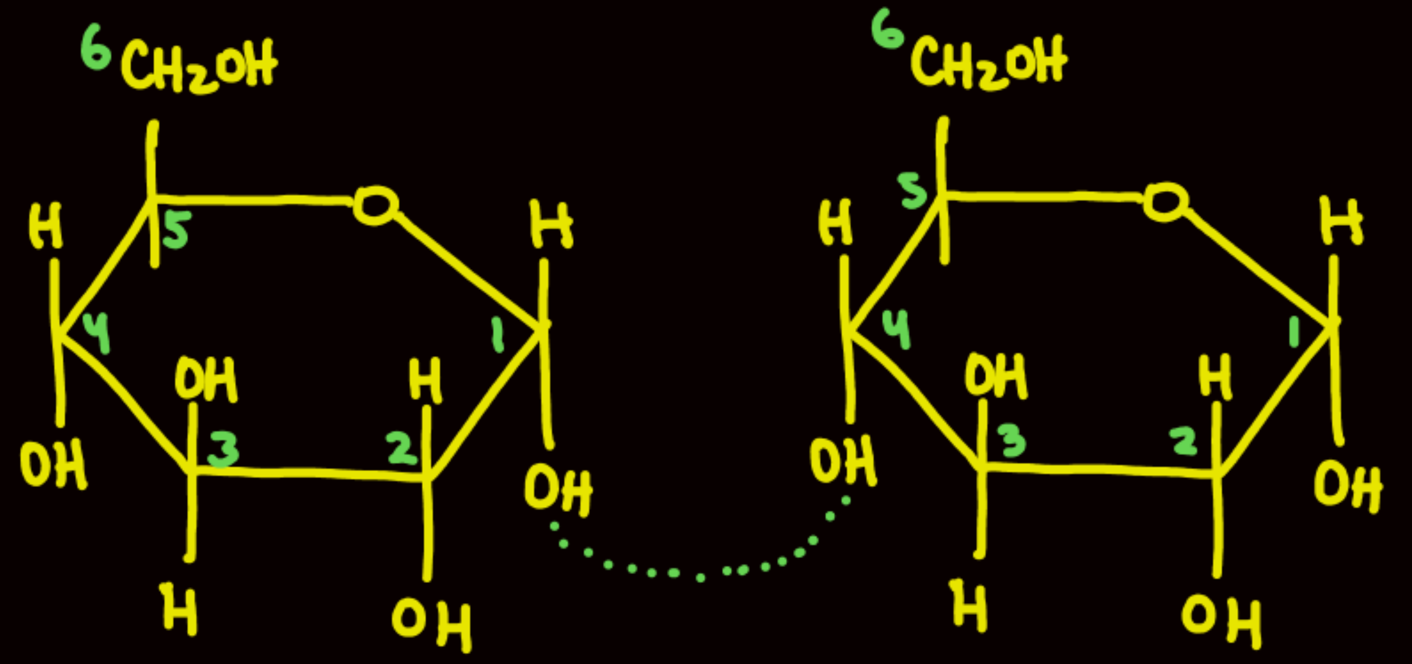
→ Produces Two Carbohydrate on Hydrolysis.

1. Maltose $\xrightarrow{H_3O^+}$ Glucose ✓ + Glucose ✓

2. Sucrose $\xrightarrow{H_3O^+}$ Glucose ✓ + Fructose ✓

3. Lactose $\xrightarrow{H_3O}$ Glucose ✓ + Galactose ✓

Maltose



α-D Glucose

α-D Glucose

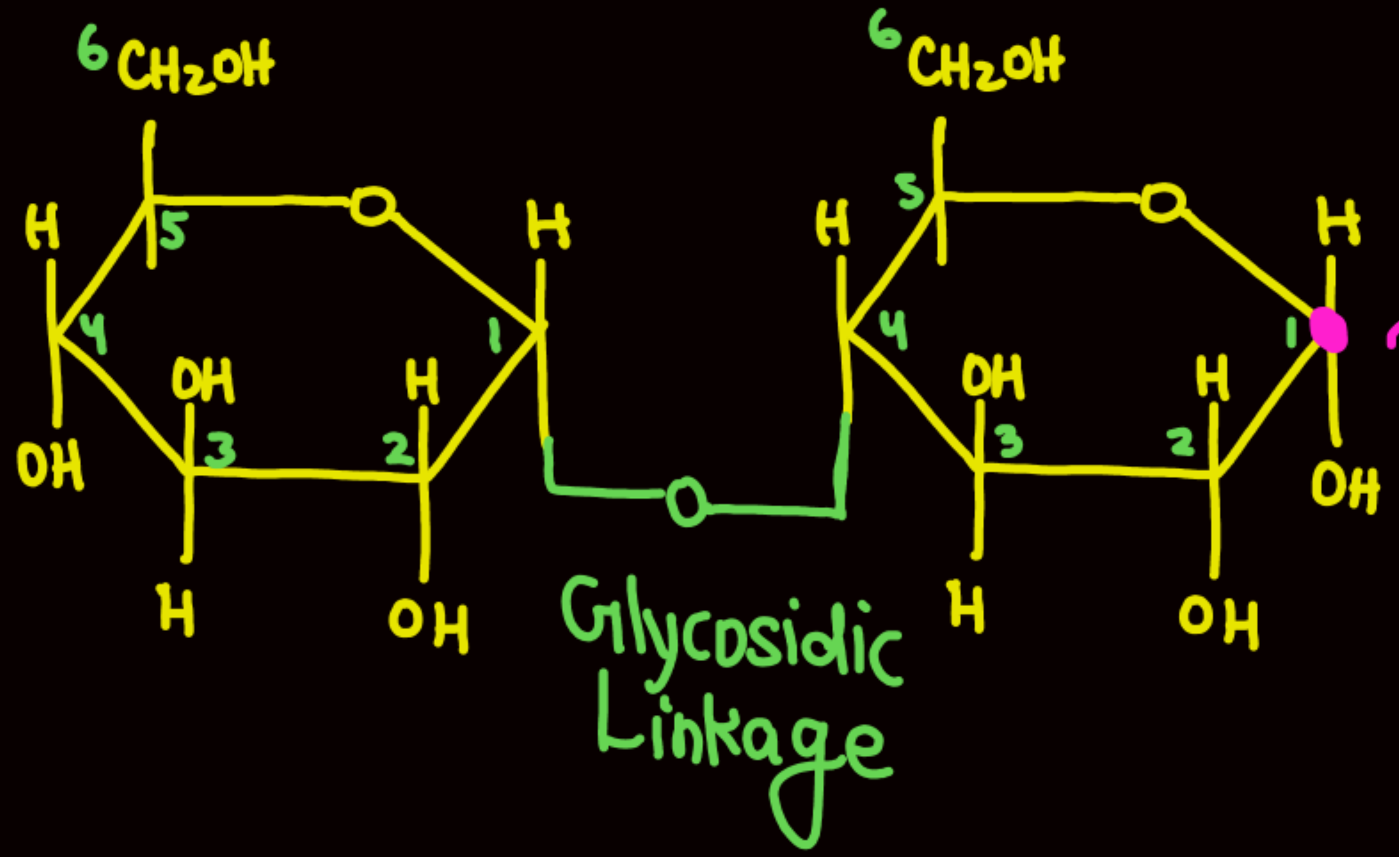
C_1 of α D Glucose

&

C_4 of α D Glucose

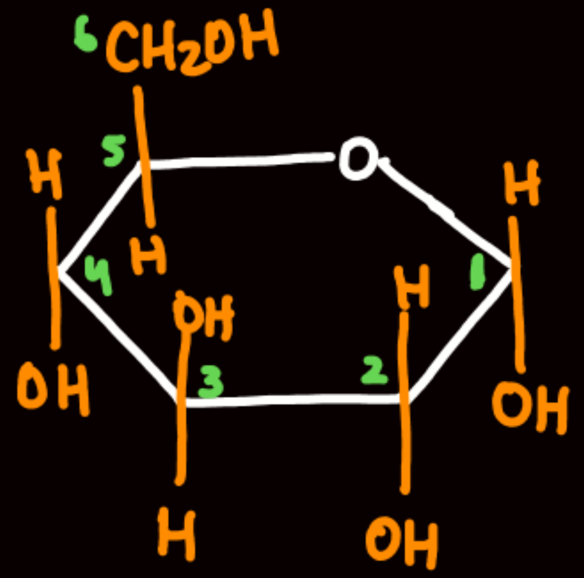
⇓

Maltose

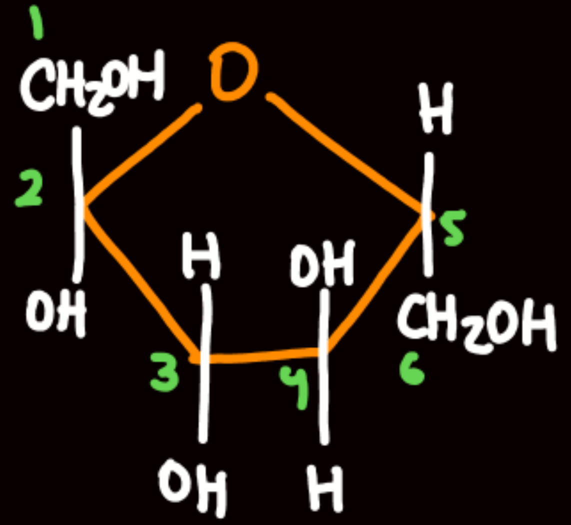


anomeric carbon has H & OH } Reducing

Sucrose

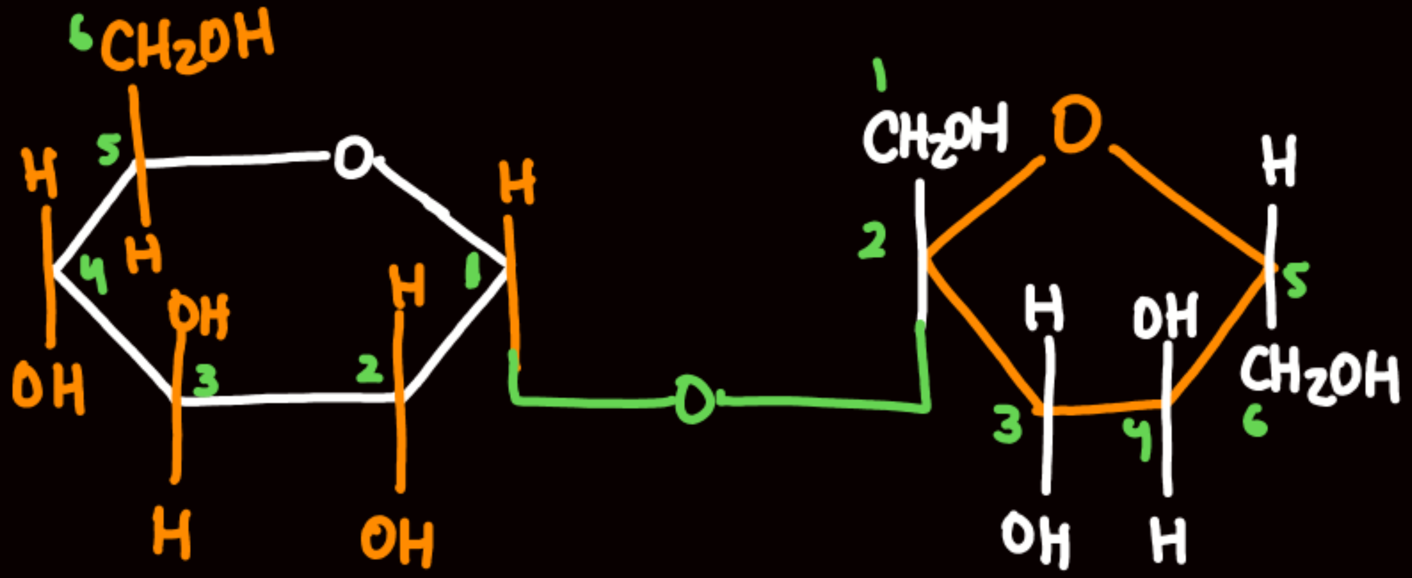


α-D Glucose



β-D Fructose

C_1 of α-D Glucose
&
C_2 of β-D Fructose
⇓
Sucrose



α-D Glucose β-D Fructose

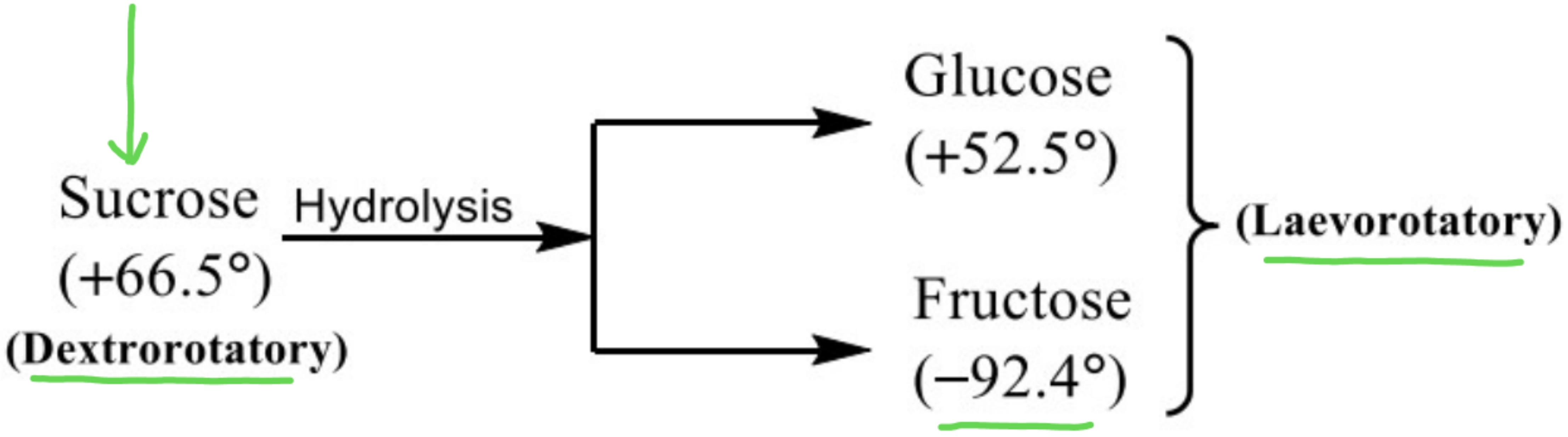
Lactose

C_1 of α D Glucose
C_4 of α D Galactose

} Glycocydic linkage

DISACCHARIDES

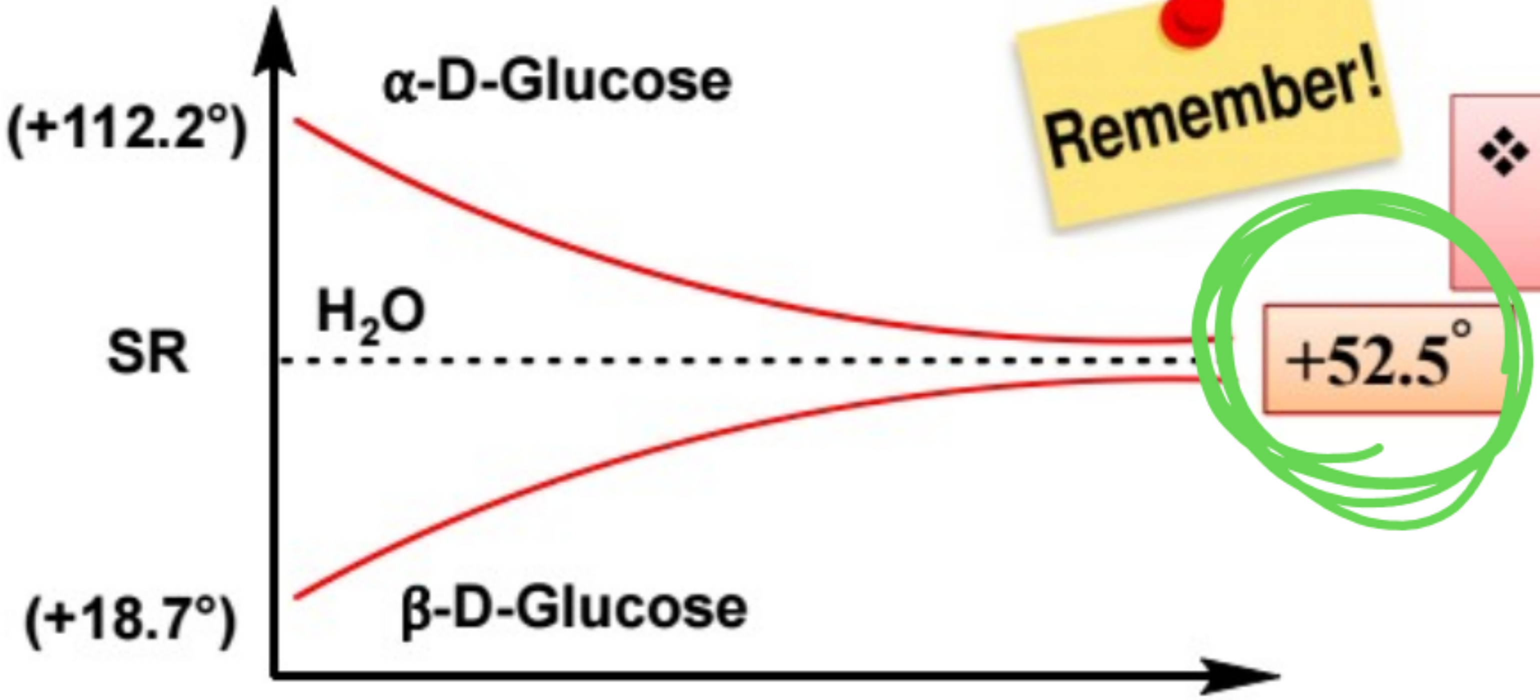
Invert Sugar



"Hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (□) and the product is named as invert sugar."

Mutarotation:

The α- & β- glucose have different specific rotations. When either is dissolved in water, their specific rotation changes to reach a certain fixed value (+52.5°). This is called **Mutarotation.**



Remember!

❖ **All reducing sugar show mutarotation.**

$$\alpha\text{-D-Glucose} \rightleftharpoons \text{Equilibrium mixture} \rightleftharpoons \beta\text{-D-Glucose}$$

Sp. rot.⇒ (+112.2°) | +52.5° | (+18.7°)